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RECENT DEVELOPMENTS IN DESULFURIZATION OF FUEL OIL AND WASTE GAS IN JAPAN-1973

Jumpei Ando

Processes Research, Incorporated

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The report documents development, demonstration, and control activities currently in progress in Japan on Japanese processes pertaining to SO2 recovery from waste gases. It also discusses hydrodesulfurization of heavy oils and gasification desulfurization of heavy and residual oils in Japan. It presents process description, state of development, advantages, disadvantages, economics, and flow sheets for 28 processes (4 dry and 24 wet) for SO2 removal and recovery from waste gases, with less detailed information on 9 other processes. The trend in waste gas treatment is from dry to wet processes yielding salable byproducts. Most plants built in Japan for the hydrodesulfurization of heavy oil utilize the indirect, rather than the direct, process. Four processes are described for the gasification desulfurization of heavy oil and residual oil: the Ube process is included in detail, with lesser information on the other three processes.

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Foreword

The sulfur abatement policy in Japan has undergone notable changes during the past year. Restrictions on SO_2 emissions have become so rigid that heavy oil with 1% sulfur produced by topped-crude hydrodesulfurization--heretofore regarded as the most promising method--is proving unsatisfactory for large power plants. Power companies now wish to burn large amounts of crude oil, naphtha and LNG in place of heavy oil but it is not easy to do so because this requires drastic structural changes in the oil industry. To reduce sulfur in heavy oil to less than 0.5%, much effort has been made recently to develop gasification desulfurization.

Waste-gas desulfurization has continued to grow remarkably. At present, about sixty commercial and prototype plants ranging in unit capacity from 50,000 to 250,000scfm and many other smaller plants are in operation. The reliability of waste-gas desulfurization, especially that by the wet process, has been generally recognized, thus prompting power companies to plan many larger commercial plants based on this process.

The present paper describes the recent developments in desulfurization efforts in Japan up to March 1973 with emphasis on waste-gas desulfurization.

April 1973

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Recent Developments in Desulfurization of Fuel Oil and Waste gas in Japan (1973)

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Remarks

The units of measurements and costs are expressed in the American way using inches, feet, gallons, barrels, grains, pounds, tons (short tons), cents, dollars, etc.

The exchange rate, $1 = ¥308, is used.

Abbreviations

BPSD:	Barrels per stream day	gal.:	Gallon, gallons
BPCD:	Barrels per calendar day	in.:	Inch, inches
MW:	Megawatts	lb:	Pound, pounds
scf:	Standard cubic feet	bl:	Barrel
scfm:	Standard cubic feet per minute	bbl:	Barrels
acfm:	Actual cubic feet per minute	t:	Ton, tons
L/G:	Liquid/gas ratio (gallons/1,000scfm)		

1 Fuel and regulation of SO_2 in Japan

1.1 Supply of energy

Energy supply in Japan is characterized by its rapid increase and heavy dependence on imported oil. The annual increases averaged 11% during the past several years (Table 1.1). Per-capita energy consumption in Japan was one-fifth that in the United States in 1965 and one-third in 1971. Consumption per acre of level land is now about eight times that in the U.S. and may be the highest in the world, resulting in serious environmental problems.

Table 1.1 Supply of primary energy (10^{12}kcal)$^{2)}$

	1965	1967	1969	1971	1975 (estimate)
Electric power					
Hydraulic	187	170	188	213	212
Nuclear	0	2	3	20	102
Coal					
Domestic	316	296	285	203	226
Imported	136	209	333	357	627
Oil					
Domestic	7	8	8	8	8
Imported	959	1,319	1,840	2,349	3,425
Natural gas					
Domestic	20	22	26	27	29
Imported (LNG)	0	0	2	13	45
Other energy sources	29	29	22	16	17
Total	1,656	2,055	2,707	3,206	4,704

Oil imports have increased at a rate of about 20% yearly. In 1971, 73% of Japan's total energy supply depended upon imported oil. Coal for fuel has been decreasing; imported coal which is on the increase is used to produce coke for the steel industry. Even though supply of nuclear energy and import of LNG (liquefied natural gas) are increasing, the dependence on petroleum is likely to keep growing for some time to come.

1.2 Oil and sulfur

Most of imported oil is in the form of crude oil. About 80% of the crude oil comes from the Middle East and is rich in sulfur. As oil companies are seeking low-sulfur oil, the average sulfur content in imported oil decreased from 1.93% in 1967 to 1.56% in 1971. Still the total amount of sulfur present in imported oil reached nearly 4 million tons in 1971.

Table 1.2.1 Crude oil imports and their sources (in million of barrels)[2)]

District	1967	1969	1971
Middle East	717.7	959.2	1,184.4
Far East	52.2	122.6	193.1
U.S.S.R.	10.7	3.8	3.1
Other districts	6.3	12.6	30.2
Total	786.9	1,098.2	1,410.8

In Japan, most of crude oil is treated by topping (atmospheric distillation). The residual oil from topping is known as "heavy oil" and is used for fuel. From 100 parts crude, 55 parts heavy oil is obtained on the average. Approximately 90% of the sulfur in crude remains in heavy oil. Heavy oil from Khafji crude has a sulfur content as high as 4%.

Consumption of heavy oil amounted to 441 million barrels in 1967 and to 745 million barrels in 1971. In 1971, about one-fourth of the heavy oil was subjected to hydrodesulfurization giving 287,000 tons of sulfur as by-product. Still nearly 3 million tons of sulfur in heavy oil burned produced nearly 6 million tons of SO_2, constituting the chief source of SO_2 emissions.

About 30% of heavy oil was burned in electric power stations and the rest in other plants and buildings (Table 1.2.2). In 1970, about 24% of the total SO_2 emission was derived from power stations, 19% from the steel industry, 16% from the ceramic industry, 15% from the chemical industry, and the rest from other sources.

Table 1.2.2 Consumption of heavy oil (in millions of barrels)[2)]

	1967	1969	1971
Electric power	119.3	187.5	222.9
Chemical industry	45.9	53.6	79.4
Steel industry	44.7	58.3	76.0
Ceramic industry	50.6	61.1	66.4
Other uses	180.1	250.3	299.8
Total	440.6	610.8	744.5

1.3 Ambient and emission standards for SO_2[3)]

The ambient standard for SO_2 has been set out as follows:

1) The hourly average SO_2 concentration should not exceed 0.2ppm in not less than 99% of the total number of hours in a given year.
2) The daily average SO_2 concentration should not exceed 0.05ppm in not less than 70% of the total number of days in a given year.
3) The hourly average SO_2 concentration should not exceed 0.05ppm in not less than 88% of the total number of hours in a given year.
4) The yearly average of hourly concentrations should not exceed 0.05ppm.

In many industrial districts and in some large cities, SO_2 concentration exceeds the standard. The time limit to attain the standard was first set for 1978 and this was recently moved up to 1975. Moreover, the standard itself might be tightened in near future.

The emission standard is given by the following equation:

$$q = k \times 10^{-3} He^2$$

q: amount of sulfur oxides, Nm^3/hr ($1Nm^3/hr = 0.59scfm$)

k: the value shown in Table 1.3.1

He: effective height of stack, meters (1 meter = 3.3ft)

Table 1.3.1 The values of k

	For existing plants		For new plants	
	before 1971	after 1972	before 1971	after 1972
Tokyo, Yokohama, etc.	11.7	6.42	5.26	2.92
Chiba, Ichihara, etc.	12.8	7.59	5.26	3.50
Kitakyushu, etc.	14.0	7.59	5.26	3.50
Omuta, etc.	17.5	9.34		5.26

As shown in Table 1.3.1 the k values were lowered in 1972 to meet the stringent ambient standard. The smallest value 2.92 has been set for new plants in such districts as Tokyo, Yokohama, etc. This means that a 1,000MW plant in these districts with an effective stack height of 1,000 feet (actual height about 400 feet) is required to use oil with less than 0.25% sulfur.

The emission standard allows smaller consumers to use fuel with higher sulfur contents. However, there are regulations on sulfur content of oil enforced in specific areas in addition to the above national standards. For example, an ordinance issued by the governer of Tokyo is shown in Table 1.3.2.

Table 1.3.2 Ordinance on sulfur content of fuel oil (Tokyo)

	Plants		Buildings	
	Consumption of oil (liters/day)*	Maximum S (%)	Consumption of oil (liters/day)	Maximum S (%)
City area	1,000 to 4,000	1.3(1.5)**	300 to 10,000	1.0(1.3)*
	4,000 to 10,000	1.0(1.3)	over 10,000	0.5(1.0)
	over 10,000	0.5(1.3)		
Other areas	1,000 to 10,000	1.3(1.7)	300 to 10,000	1.0(1.3)
	over 10,000	1.0(1.3)	over 10,000	0.5(1.0)

* 1,000 liters = 6.29 barrels 10,000ℓ/day is equivalent to 1.6MW.

** Parenthesized figures are for existing plants and buildings. Other figures are for those to be newly built.

1.4 Sulfur abatement policy of government[3)]

The targets for sulfur redu [illegible] ve been established from the viewpoint of achieving and mai [illegible] g the environmental quality standards for sulfur oxides. Three types of areas requiring countermeasures have been differentiated for the purpose of establishing the targets(Table 1.6). Excessively populated areas are defined as having excessive population and extremely polluted air due to the disorderly establishment of industries. Polluted areas are not populated excessively but suffer from pollution which exceeds environmental quality standards. Threatened areas require preventive measures due to the possibility of pollution exceeding environmental quality standards if the sulfur content of fuels is not reduced. The number of threatened areas is expected to increase in the future.

Average sulfur content of all fuels for industry, general public requirements and other sectors should be lowered from the 2.5% of 1967 to 1.5% in 1973 and 1.15% in 1978.

Table 1.4 Targets for sulfur reduction

	1967		1973		1978	
	Quantity (millions of bbl)	Sulfur (%)	Quantity (millions of bbl)	Sulfur (%)	Quantity (millions of bbl)	Sulfur (%)
Excessively polluted areas	144.5	2.41	274.2	0.90	346.0	0.55
Polluted areas	82.2	2.51	178.0	1.30	289.3	0.80
Threatened areas	-	-	173.0	1.45	340.0	1.00
All sectors of the economy	401.9	2.5	976.2	1.50	1,383.8	1.15

1 Heavy oil, raw crude oil for combustion and liquefied natural gas are included in fuels. Quantities are given in terms of heavy oil.

2 Sulfur contents have been adjusted after taking into consideration the effects of flue-gas desulfurization, which is substantially equal to the reduction of sulfur content in fuels by means of desulfurizing of heavy oil.

More rapid sulfur abatement than is shown in Table 1.4 may be required because of the situation of the ambient standard as was described in 1.3.

In order to attain these goals, several methods have been employed including the lowering of sulfur content of imported crude oil, import of LNG, desulfurization of heavy oil and waste gas. The Agency of Industrial Science and Technology, MITI, awarded contracts to several groups for the development of processes for flue-gas desulfurization (dry processes) and heavy-oil desulfurization (topped-crude hydrodesulfurization) expending 8.5 million dollars between 1966 and 1971. MITI has recently set up a new program for the development of "closed systems." Under this program financial aid has been awarded to Ube Industries for the development of gasification desulfurization of heavy oil which will be described in 3.2.

MITI has been helping oil companies to promote hydrodesulfurization of heavy oil by paying them $0.26/bl heavy oil subjected to the treatment. MITI is advising industries to increase the capacity of hydrodesulfurization to a million BPSD and that of flue-gas desulfurization to 4,300MW by 1975.

1.5 Trends in fuels and their desulfurization

Fuels consumed in power plants are shown in Table 1.5.1. The use of coal has decreased. Although low-sulfur fuels--crude oil for direct combustion and LNG and natural gas--have been used in increasing amounts, the use of heavy oil has increased markedly.

Table 1.5.1 Fuels consumed by power companies*2)

	1967	1969	1971
Heavy oil (millions of barrels)	119.3	187.5	222.9
Crude oil (millions of barrels)	13.8	24.8	69.2
Coal (millions of tons)	28.8	26.8	15.3
LNG (millions of tons)	0	0.1	0.8
Natural gas (billions of scf)	0.2	0.1	4.6

* These companies produce 87% of Japan's total electric power.

Until recently, topped-crude hydrodesulfurization of heavy oil by which sulfur is reduced from 4 to 1% was considered to be the most promising way of desulfurization. The present stringent regulation on SO_2 emissions, however, rendered oil with 1% sulfur unsatisfactory for new power plants. Even for existing plants, restrictions on SO_2 emissions which are more stringent than official regulations are compeled by inhabitants. Under such situation, major power companies plan to use large amounts of low-sulfur fuels such as crude oil, naphtha and LNG replacing heavy oil (Table 1.5.2).

Table 1.5.2 Use of fuels by nine major power companies*[2)]

	Used		Planned			
	1971	1972	1973	1974	1975	1976
Coal (millions of tons)	9.6	6.7	4.7	4.4	4.1	3.3
Heavy oil (millions of barrels)	183.7	187.3	146.6	134.3	114.4	116.1
Crude oil (millions of barrels)	69.1	112.7	188.9	221.7	254.5	274.0
Naphtha (millions of barrels)	0	1.9	15.4	44.0	60.3	67.3
LNG (millions of tons)	0.8	0.8	1.4	2.5	3.9	4.8
Natural gas (billions of scf)	4.6	6.0	6.4	6.7	7.3	7.9
LGL (millions of barrels)	0	0	2.8	3.4	4.7	4.7
Total (millions of barrels in terms of heavy oil)	284.9	323.9	367.5	416.9	454.1	483.7
Flue-gas desulfurization (MW)	110	357		2,700	3,700	4,800

* These companies produce 71% of Japan's total electric power.

Oil companies oppose the plan of the power companies because drastic changes in the oil refineries will be required to carry out the plan. The oil companies are now much interested in gasification desulfurization of heavy oil by which sulfur can be reduced to 0.2% and are trying to build commercial plants to supply the gas to power stations.

Waste-gas desulfurization has developed remarkably, with more than sixty commercial and prototype plants now in operation. Most of the plants built so far are of relatively small capacity and designed to treat waste gas from industrial boilers, chemical and smelting plants, etc. Major power companies have recently decided to build larger plants. The total capacity of the desulfurization plants of the major power companies will increase from the 357MW in 1972 to 2,700MW in 1974 and to 4,800MW in 1976 (Table 1.5.2). Further increases in capacity will be needed because in 1976 it will still be only 6% of the total power capacity 8,000,000MW.

2 Hydrodesulfurization of heavy oil

Many hydrodesulfurization plants have been built since 1967 by oil companies in various districts of Japan (Tables 2.1 and 2.2). Four of them use the topped-crude desulfurization process (or the atmospheric residual desulfurization process which is often referred to as the direct process) and others the vacuum gas-oil desulfurization process (indirect process). By the direct process, sulfur in oil can be reduced from 4% to 1% (Figure 2.1) but the life of catalyst is a problem. Moreover, product oil containing 1% sulfur will be unsatisfactory for large power plants to be built. Although four other plants are under construction at present (Table 2.2), it is unlikely that many plants will be constructed in future. Among the four plants in operation, two use the UOP process (Figures 2.3 and 2.4),the other two use the Gulf process (Figure 2.5), both of which are equipped with fixed-bed reactors. These plants have been operated for about 60% of the total hours in 1972 on the average. Pilot plant tests have been carried out by the Government Chemical Research Institute with a moving-bed reactor and by Nippon Oil with suspended-bed reactors. All of these processes were described in detail by the present author in his 1972 report.[1] There has been no remarkable development in these processes during the past year.

By the indirect process, heavy oil is first distilled under vacuum. The distillate (vacuum gas oil) is desulfurized down to 0.2% sulfur without significant technical trouble (Figures 2.2 and 2.6). The desulfurized oil is normally mixed with the residue of vacuum distillation which is difficult to be desulfurized. The mixed oil contains 2.4% sulfur when heavy oil with 4.0% sulfur is treated and is not satisfactory to meet the requirements for SO_2 control. Therefore, it is desirable to use the desulfurized vacuum gas oil with 0.20% sulfur for fuel and the residual oil for other purposes. One of the promising ways of utilizing the residual oil is thermal decomposition with the gasification desulfurization as will be described in the following chapter.

The amounts of sulfur by-produced from hydrodesulfurization of heavy oil annually from 1968 to 1975 are shown in Table 2.3. The amount of recovered sulfur in 1972 was less than expected due to the fewer operation hours of topped-crude desulfurization plants, resulting in a temporary shortage of sulfur in Japan.

Table 2.1 Hydrodesulfurization plants built by 1971

Refiner	Plant site	Process	Completed	Capacity(per day)	
				Oil(BPSD)	Sulfur(tons)
Idemitsu Kosan	Chiba	UOP*	1967	40,000	265
Fuji Oil	Sodegaura	CRC	1968	23,000	100
Toa Nenryo	Wakayama	ER&E	1968	25,000	180
Daikyo Oil	Umaokoshi	Gulf	1969	17,500	110
Nippon Oil	Negishi	CRC	1969	40,000	190
Showa Oil	Kawasaki	Shell	1969	16,000	66
Kyushu Oil	Oita	Shell	1969	14,000	55
Mitsubishi Oil	Mizushima	UOP	1969	30,000	100
Maruzen Oil	Chiba	Union	1969	35,000	165
Seibu Oil	Yamaguchi	Shell	1969	4,000	28
Nippon Mining	Mizushima	Gulf*	1970	27,760	165
Koa Oil	Marifu	CRC	1970	8,000	39
General Oil	Sakai	ER&E	1970	31,000	73
Kashima Oil	Kashima	UOP*	1970	45,000	265
Daikyo Oil	Umaokoshi	Gulf	1970	17,500	77
Kansai Oil	Sakai	ER&E	1971	20,000	88
Koa Oil	Osaka	CRC	1971	12,000	55
Toa Nenryo	Kawasaki	ER&E	1971	51,000	220
Total				456,260	2,241

* Topped-crude hydrodesulfurization processes; those without asterisks are for vacuum gas-oil hydrodesulfurization.

Table 2.2 Hydrodesulfurization plants built after 1971

Refiner	Plant site	Process	Year of completion	Capacity oil (BPSD)
Nippon Oil	Negishi	CRC	1972	28,000
Idemitsu Kosan	Himeji	Gulf*	1972	40,000
Kyokuto Petroleum	Chiba	UOP	1972	60,000
Toa Nenryo	Kawasaki	ER&E	1972	9,000
Asia Kyoseki	Sakaide	CRC	1972	15,000
Kyushu Oil	Oita	UOP	1972	25,000
Showa Yokkaichi Oil	Yokkaichi	Shell	1972	35,000
Seibu Oil	Yamaguchi	Shell	1972	1,000
Nippon Oil	Muroran	CRC	1973	40,000
Toa Oil	Nagoya	CRC	1973	30,000
Nippon Mining	Mizushima	Gulf*	1974	3,240
Toa Nenryo	Wakayama	ER&E*	1974	45,000
Toa Oil	Nagoya		1974	37,000
Kansai Oil	Sakai	ER&E*	1974	40,000
Showa Yokkaichi Oil	Yokkaichi	Shell	1974	5,000
Mitsubishi Oil	Mizushima	UOP*	1975	45,000
Total				469,240

* Topped-crude hydrodesulfurization; those without asterisks are for vacuum gas-oil hydrodesulfurization

Table 2.3 Amount of sulfur recovered by hydrodesulfurization of heavy oil (tons)4)

	1969	1970	1971	1972	1973*	1974*	1975*
Topped-crude desulfurization					259	376	502
Vacuum gas-oil desulfurization					387	414	425
Total	74	171	287	511	646	790	927

* Estimated values assuming 6,600 hours' operation for topped-crude desulfurization plants and 7,000 hours' operation for vacuum gas-oil desulfurization plants in a year.

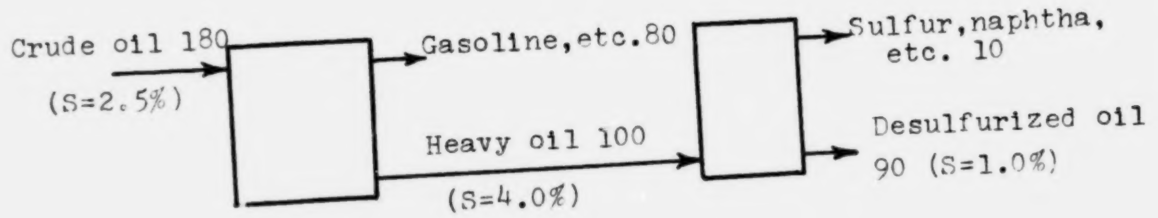

Crude oil 180
(S=2.5%)
Gasoline,etc.80
Heavy oil 100
(S=4.0%)
Sulfur,naphtha,
etc. 10
Desulfurized oil
90 (S=1.0%)

Figure 2.1 Rough material balance in topping and topped-crude hydrodesulfurization (direct process)

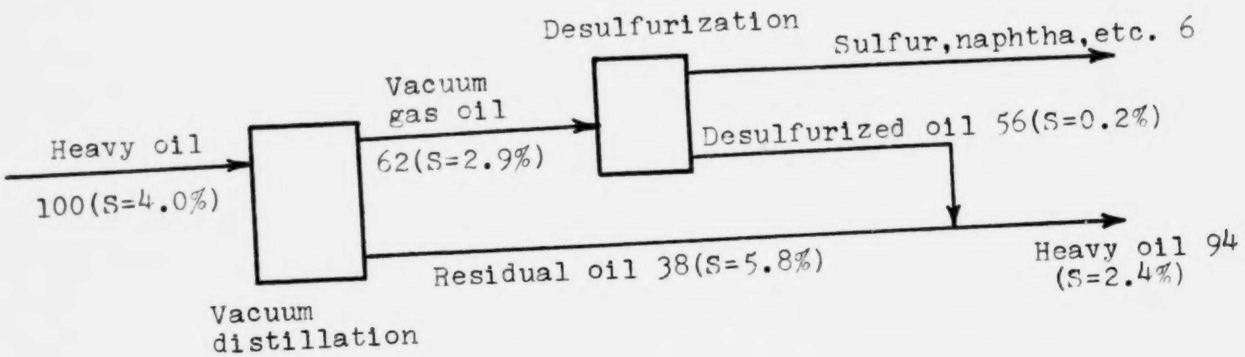
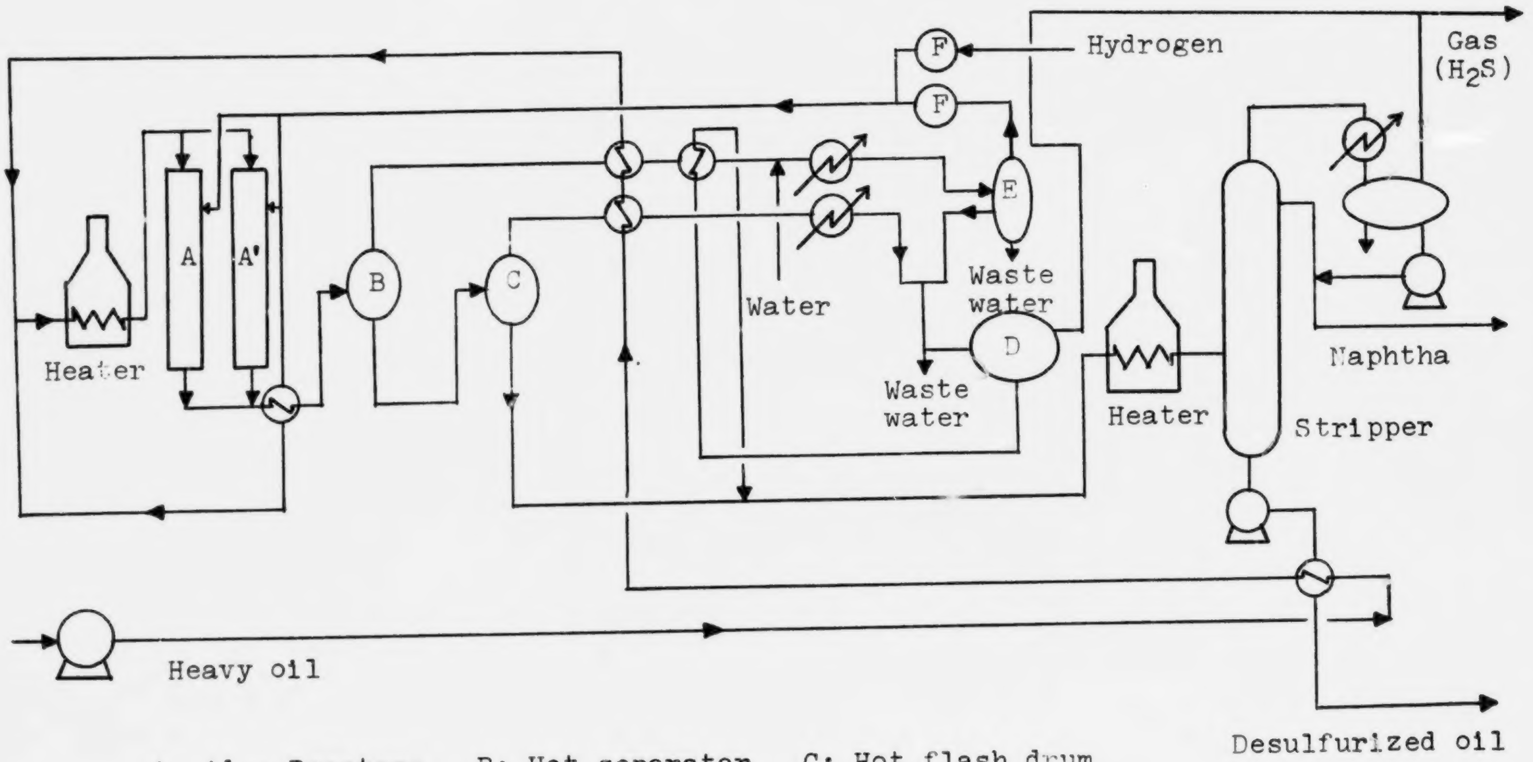

Heavy oil
100(S=4.0%)
Vacuum
distillation
Vacuum
gas oil
62(S=2.9%)
Desulfurization
Sulfur,naphtha,etc. 6
Desulfurized oil 56(S=0.2%)
Residual oil 38(S=5.8%)
Heavy oil 94
(S=2.4%)

Figure 2.2 Rough material balance in vacuum gas-oil hydrodesulfurization (indirect process)


Gas
(H_2S)
Hydrogen
F
F
E
Waste water
D
Waste water
Water
Heater
A
A'
B
C
Heater
Stripper
Naphtha
Heavy oil
Desulfurized oil

A, A' : Reactors B: Hot separator C: Hot flash drum
D: Cold flash drum E: Cold separator F: Compressor

Figure 2.3 Flow sheet of UOP (RCD) Isomax process

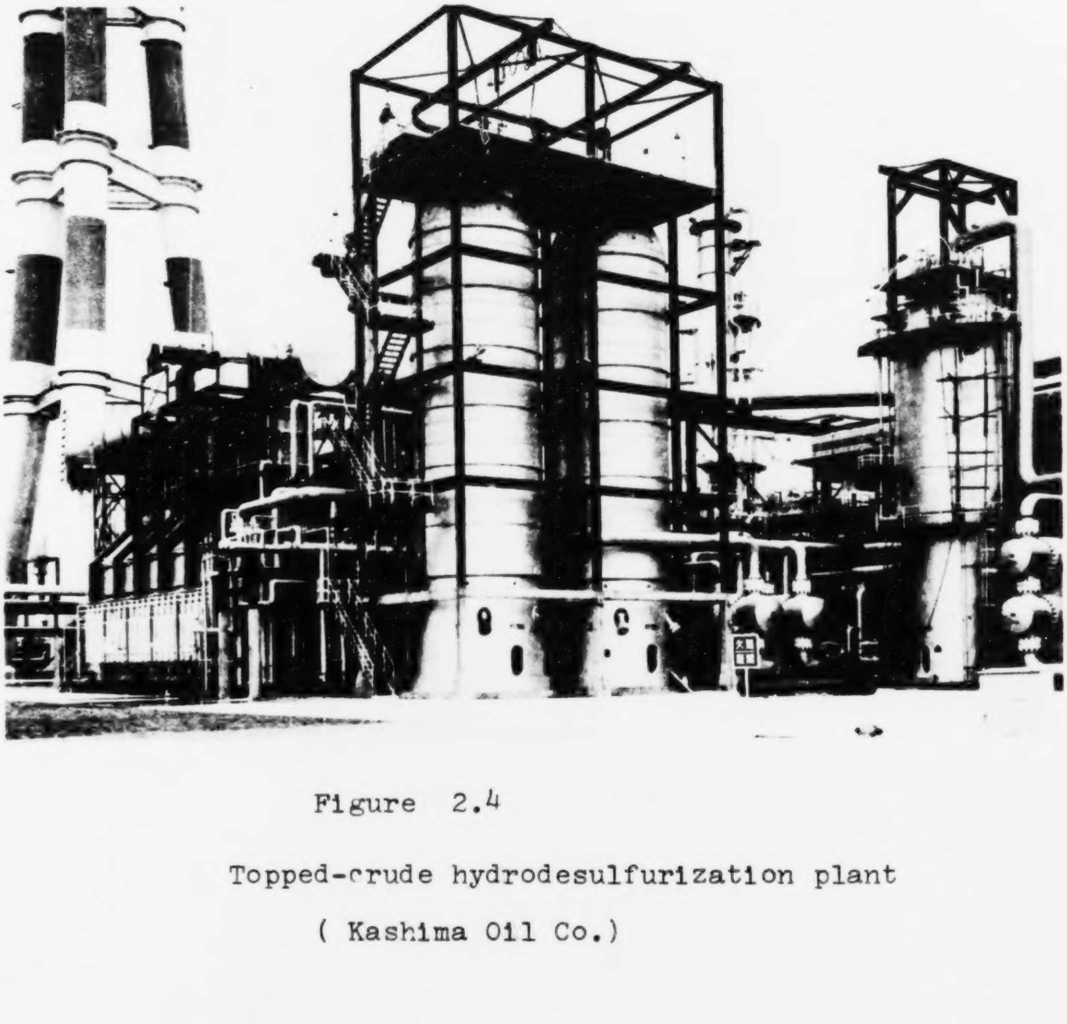


Figure 2.4

Topped-crude hydrodesulfurization plant

(Kashima Oil Co.)

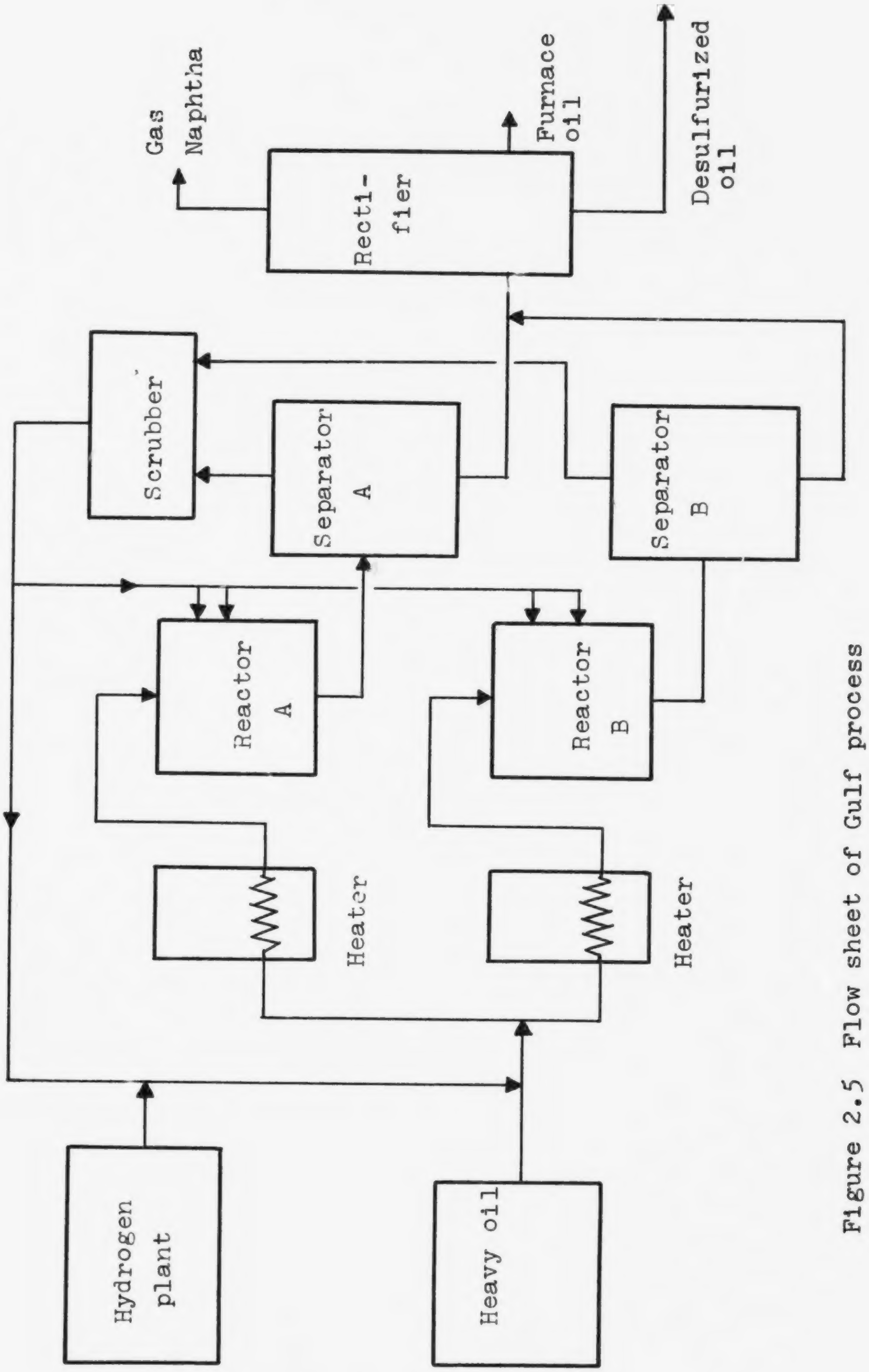
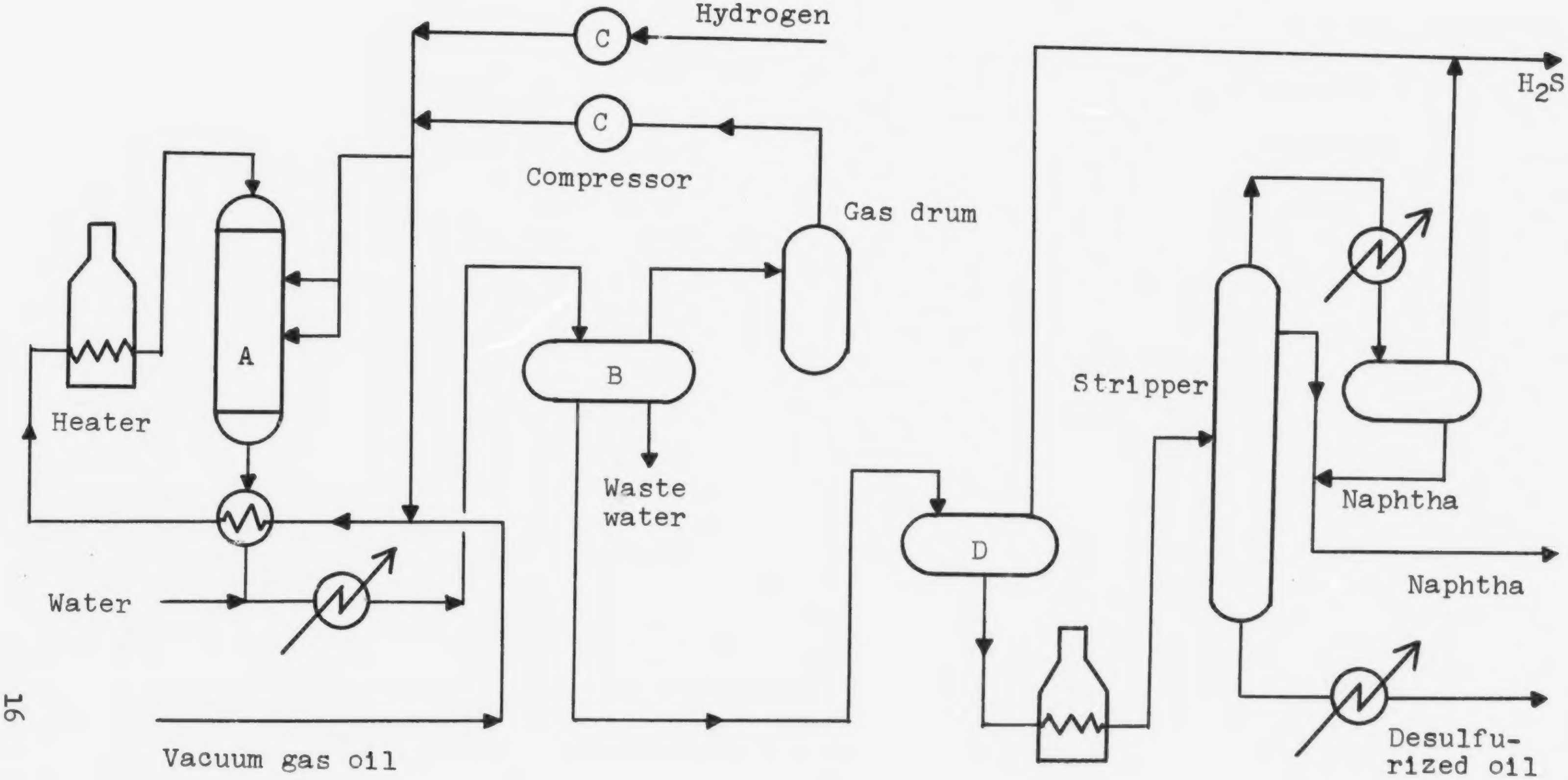

Hydrogen plant
Heavy oil
Heater
Heater
Reactor A
Reactor B
Scrubber
Separator A
Separator B
Recti-fier
Gas
Naphtha
Furnace oil
Desulfurized oil

Figure 2.5 Flow sheet of Gulf process


Hydrogen
C
C
Compressor
Gas drum
H_2S
A
Heater
B
Waste water
Water
Stripper
D
Naphtha
Naphtha
Vacuum gas oil
Desulfurized oil

A: Reactor   B: High pressure separator   D: Low pressure separator

Figure 2.6 Vacuum gas-oil desulfurization process

3 Gasification desulfurization of heavy oil and residual oil

3.1 Outline

Gasification desulfurization of heavy oil and residual oil from vacuum distillation has been recently considered an important means of producing low-sulfur fuel since the demand for fuels containing less than 1% sulfur has increased sharply. Toa Oil Co. has decided to adopt the Flexicoking process developed by ER&E, USA. A plant with a capacity of treating 18,000BPSD of oil will be completed in Kawasaki by early 1975. Other oil companies, Toa Nenryo, General Oil, Asia Oil, Idemitsu Kosan, Nippon Oil, etc. are also interested in gasification desulfurization. Two chemical companies, Ube Industries and Kureha Chemical Industries, have developed their own process.

By the Ube process virtually all of the feed oil is converted to a fuel gas with a very low sulfur content (0.02%). Much oxygen is required in this case. On the other hand, by the Flexicoking process residual oil from vacuum distillation of heavy oil is subjected to thermal decomposition to obtain fuel oil with a relatively low sulfur content and the remaining tar or coke which is rich in sulfur is gasified and desulfurized. This process may be less expensive consuming as it does less oxygen, but overall sulfur removal is not as high as by the Ube process. Both the cost and the desulfurization ratio vary with the degree of gasification.

An example of the process to reduce sulfur to 0.2% is shown in Figure 3.1.1.5) Heavy oil is first distilled under vacuum. Most of the residual oil is heated to 500°C to be decomposed into gas, oil, tar, and a small amount of coke. The oil from the decomposition step is subjected to hydrodesulfurization together with the distillate from the vacuum distillation. A small portion of the residual oil from the distillation is subjected to partial oxidation to produce hydrogen for the hydrodesulfurization. The tar from the decomposition step is reacted with oxygen to produce gas which is subjected to desulfurization together with the gas from the decomposition step.

From 86,200BPCD of heavy oil (31.5 million barrels per year) containing 4.1% sulfur, 70,910BPCD of liquid fuel (4.024 million tons per year) containing 0.23% sulfur and 108 million scf per day of fuel gas (722,000 tons per year in terms of heavy oil) containing 0.02% sulfur with a heat capacity 170 kilocalories per scf are obtained along with 530 tons per day of elemental sulfur. The average sulfur content of the produced fuels is 0.2%. The yield of the desulfurized fuel is 92.6%.

A cost estimation for the process is shown in Table 3.1. The cost is $1.74 per barrel of product in terms of heavy oil assuming 6,130 hours' operation in a year. The cost is higher at fewer operation hours. The process includes the gasification of about 18% of feed oil. The more the gasification the lower the sulfur content of the product and the higher the cost. The relationship of product sulfur content and cost is shown in Figure 3.1.2. The cost increases markedly as the sulfur is reduced to below 0.2%.

Table 3.1 Cost estimation for the production of low-sulfur fuel by decomposition and gasification of heavy oil as shown in Figure 3.1.1.[5)]

(Seawater for cooling 5.8 mil/t, industrial water 14.6 mil/t, pure water 175 mil/ton, electric power 16.2 mil/kWh, fuel 25.9 mil/10,000 kcal, oxygen 0.37 mil/scf, hydrogen 0.50 mil/scf, steam $2.05/t. 6,130 hours' operation in a year.)

Investment cost (millions of dollars)	
On site	89.3
Off site	35.7
Patent fee	4.8
Catalyst	1.05
Other	12.8
Total	143.65

Processing cost (millions of dollars/year)	
Fixed cost	
Depreciation	13.25
Maintenance	3.75
Labor	1.36
Management	3.86
Interest	8.52
Tax	1.27
Insurance	0.21
Subtotal	32.22
Variable cost	18.36
Total	50.58

Processing cost for one barrel (heavy oil conversion basis) equals $1.74/bl.

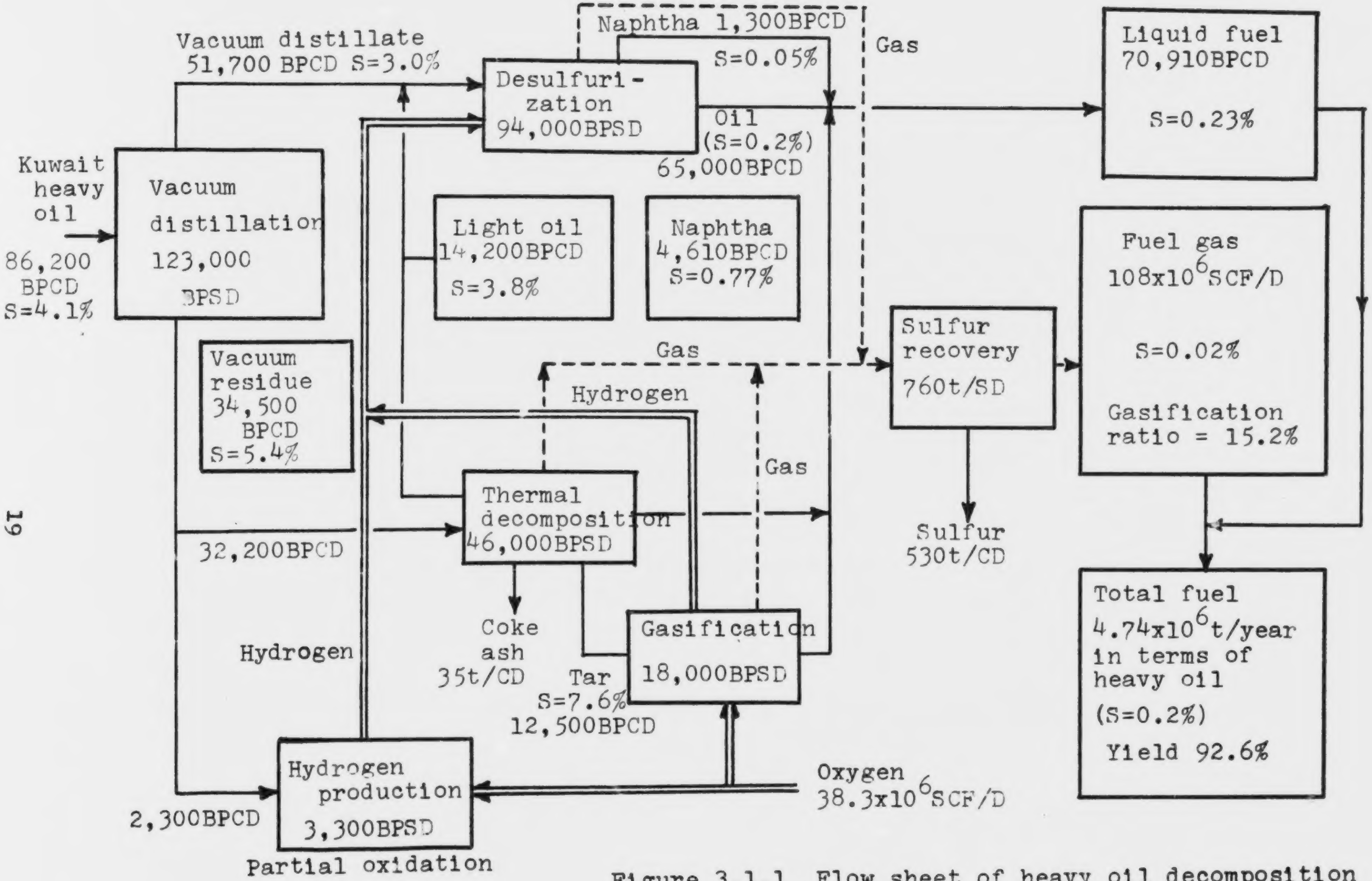

Kuwait heavy oil
86,200 BPCD S=4.1%
Vacuum distillation 123,000 BPSD
Vacuum distillate 51,700 BPCD S=3.0%
Vacuum residue 34,500 BPCD S=5.4%
32,200BPCD
2,300BPCD
Hydrogen
Hydrogen production 3,300BPSD
Partial oxidation
Desulfuri-zation 94,000BPSD
Naphtha 1,300BPCD
S=0.05%
Oil (S=0.2%) 65,000BPCD
Light oil 14,200BPCD S=3.8%
Naphtha 4,610BPCD S=0.77%
Gas
Hydrogen
Gas
Thermal decomposition 46,000BPSD
Coke ash 35t/CD
Tar S=7.6% 12,500BPCD
Gasification 18,000BPSD
Oxygen 38.3x10^6SCF/D
Gas
Sulfur recovery 760t/SD
Sulfur 530t/CD
Liquid fuel 70,910BPCD S=0.23%
Fuel gas 108x10^6SCF/D S=0.02%
Gasification ratio = 15.2%
Total fuel 4.74x10^6t/year in terms of heavy oil (S=0.2%)
Yield 92.6%

Figure 3.1.1 Flow sheet of heavy oil decomposition to produce fuel oil and gas (S=0.2%)[5)]

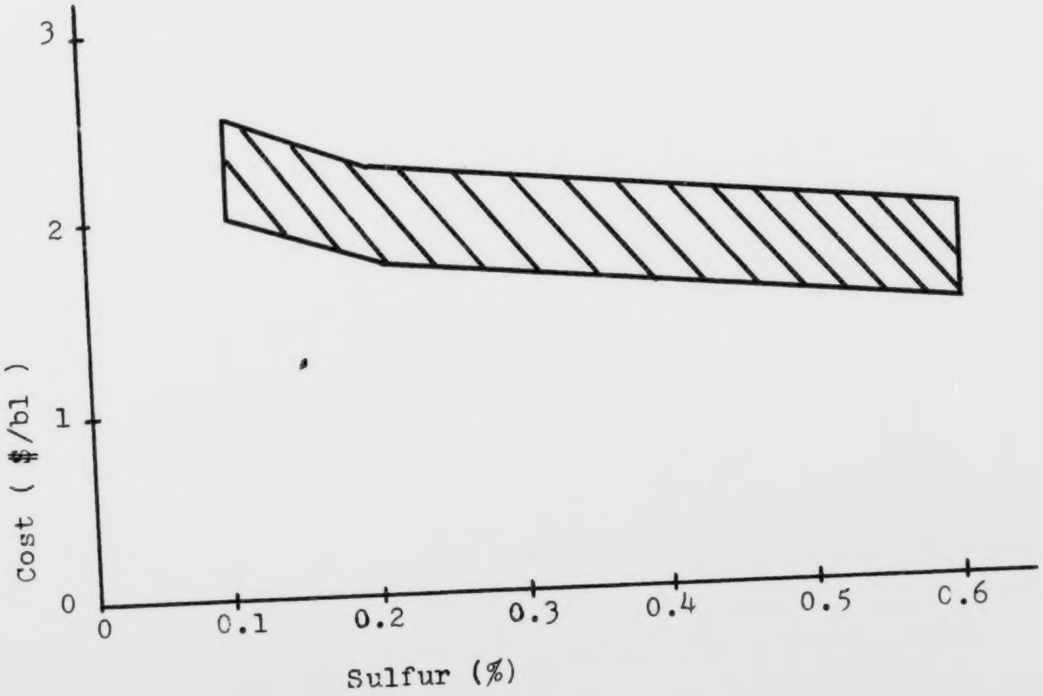


Figure 3.1.2 Processing cost of heavy oil to produce low-sulfur fuel5)

3.2 Production of fuel gas by gasification desulfurization of heavy oil (Ube process)[6]

Developer Ube Industries Ltd.
2-1, Nagatacho, Chiyoda-ku, Tokyo

Process description Heavy oil is charged into a reactor with oxygen and steam and undergoes partial oxidation at 850°C under atmospheric pressure (Figure 3.2.1). In the reactor, silica-alumina particles including an additive are fluidized to promote the gasification of heavy oil. The gas leaving the reactor is cooled to 450°C in a quencher placed above the reactor by spraying residual oil from a distillator. The silica-alumina particles are fluidized also in the quencher and are gradually coated with carbon. The carbon-coated particles are sent to a high-temperature reactor placed under the reactor. In the high-temperature reactor, the particles are fluidized to remove the carbon by reactions with oxygen and steam at 1,200°C. The cleaned silica-alumina particles go up to the reactor.

The product gas contains hydrogen, hydrocarbons, carbon oxides, hydrogen sulfide, and a small amount of sulfur dioxide (Table 3.2.1). The gas is cooled, condensed and treated in a distillator. The residual oil from the distillator is sent to the quencher and high-temperature reactor. The distillate is cooled in a condenser to separate gas oil, which is then returned to the reactor. The gas from the condenser is sent to a preabsorber, where SO_2 and a portion of H_2S in the gas is absorbed by an ammonium sulfite solution according to the following equation:

$$3(NH_4)_2SO_3 + SO_2 + 2H_2S = 3(NH_4)_2S_2O_3 + 2H_2O$$

Ammonium thiosulfate thus formed is concentrated and decomposed in a decomposer to release SO_2 and ammonia, which are sent to an IFP reactor.

$$(NH_4)_2S_2O_3 \longrightarrow S + SO_2 + 2NH_3 + H_2O$$

The gas from the preabsorber is compressed and led into a H_2S absorber, where H_2S is absorbed by a K_2CO_3 solution.

$$K_2CO_3 + H_2S \rightleftarrows KHCO_3 + KHS$$

H_2S is regenerated from the solution by heating and sent to the IFP reactor to react with SO_2 and to produce elemental sulfur.

$$2H_2S + SO_2 = 3S + 2H_2O$$

As SO_2 from the decomposer is not sufficient to react with H_2S, a portion of the by-produced sulfur is burned by air to form SO_2 which is led into the IFP reactor. Ammonia passes through the IFP reactor without reaction and is returned to the preabsorber. The composition of the gases before and after the desulfurization step is shown in Table 3.2.2.

Table 3.2.1 Material balance before and after the decomposition (by weight)

Input		Output	
Feed oil	1,000	H_2	26
Oxygen	532	CH_4	120
Steam	560	C_2H_4	216
Total	2,029	Other hydrocarbons	521
		CO	348
		CO_2	581
		O_2	2
		N_2	2
		H_2S	36
		SO_2	4.7
		Organic sulfur	1.3
		Gas oil	82.7
		Steam	450
		Total	2,092

Table 3.2.2 Composition of the gases before and after the desulfurization (volume %)

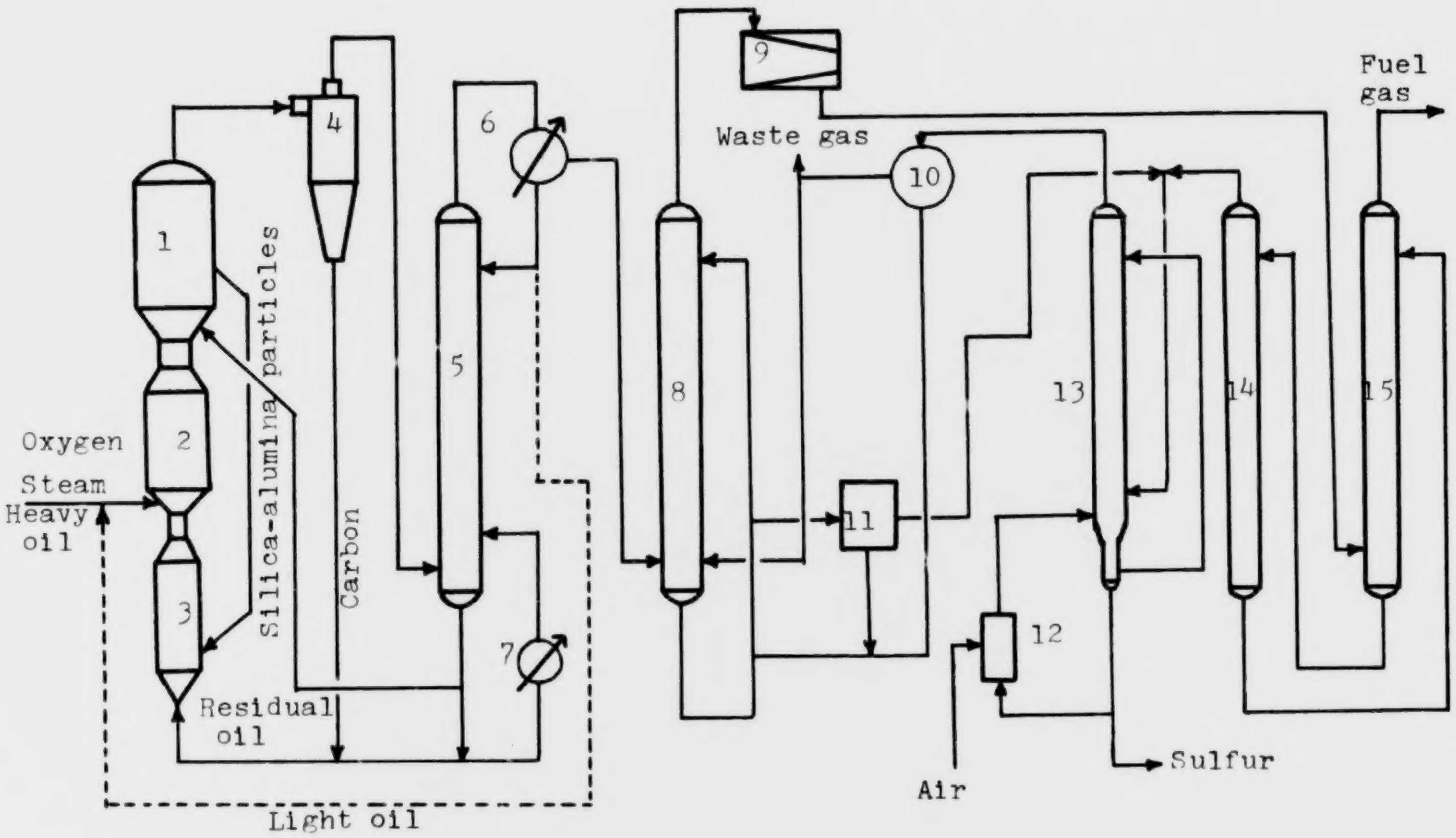
	Before desulfurization	After desulfurization
H_2	21.8	26.8
CH_4	12.5	15.3
C_2H_4	12.9	15.8
Other hydrocarbons	7.5	9.1
CO	20.7	25.4
CO_2	22.0	6.7
O_2	0.1	0.1
N_2	0.6	0.7
H_2S	1.8	0.01
SO_2	0.1	0
Organic sulfur	0.03	0.01

State of development A pilot plant to treat 55 tons of heavy oil per day has been operated since 1969. The construction of a prototype plant to treat 275 tons of heavy oil per day (40MW equivalent) was started in April 1972 with financial aid from MITI. The gasification unit of the prototype plant has been completed and is now in operation. The desulfurization unit will be completed in April 1973. A commercial plant to supply fuel gas to a 500MW plant would be equipped with six gasification units each with a capacity of treating 550 tons of heavy oil per day and a desulfurization unit.

Advantages High-sulfur heavy oil and residual oil can be utilized. More than 97% of sulfur is removed. Far smaller desulfurization facility than in flue gas desulfurization because of the smaller amount of gas with higher concentrations of sulfur compounds.

Disadvantages Much oxygen is required. Separation of H_2S from the gas containing olefines and carbon dioxide is not quite easy. The entire gasification process is not suitable for fuel supply to power plants that frequently undergo large changes of operation load because it is not easy to change the load of the gasification plant and it requires large tanks to store the gas.

Economics The prototype plant with a capacity to treat 275 tons of heavy oil per day cost $5 million including the desulfurization unit. Investment cost for a commercial plant with a capacity to treat 3,300 tons of oil per day (500MW equivalent) is estimated at $20 million including oxygen production and desulfurization units. The cost for a million kilocalories of product gas is estimated at $3.1 when the plant operation is carried out for 7,900 hours a year and about $3.4 for 6,100 hours. The relationship of cost to plant size is shown in Figure 3.2.3. Figure 3.2.3 shows that the fuel gas produced by a 500MW equivalent plant is much cheaper than LNG and can compete with naphtha in cost as well as in sulfur content.


Oxygen
Steam
Heavy oil
1
2
3
Silica-alumina particles
Residual oil
Light oil
4
Carbon
5
6
7
8
9
Waste gas
10
11
12
Air
13
Sulfur
14
15
Fuel gas

1: Quencher 2: Reactor 3: High-temperature reactor 4: Cyclone 5: Distillator
6: Condenser 7: Cooler 8: Preabsorber 9: Compressor 10: Condenser
11: Decomposer 12: Sulfur burner 13: IFP reactor 14: Regenerator 15: H_2S absorber

Figure 3.2.1 Flow sheet of Ube process

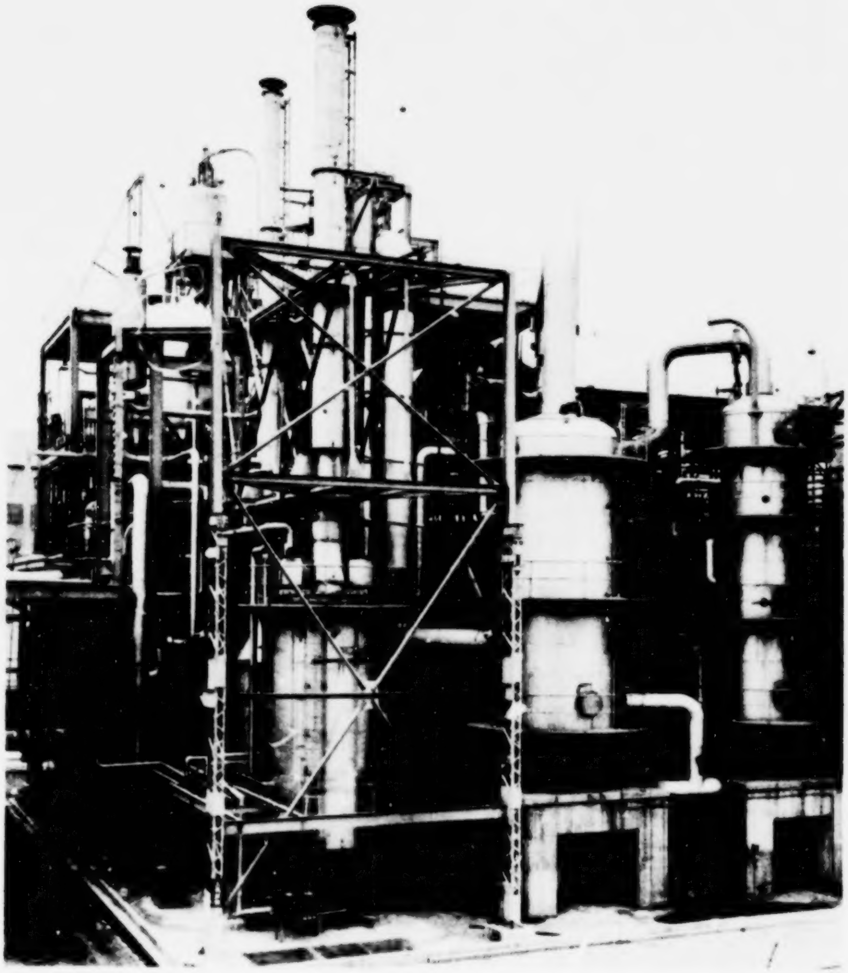


Figure 3.2.2 Prototype plant for gasification desulfurization by Ube process

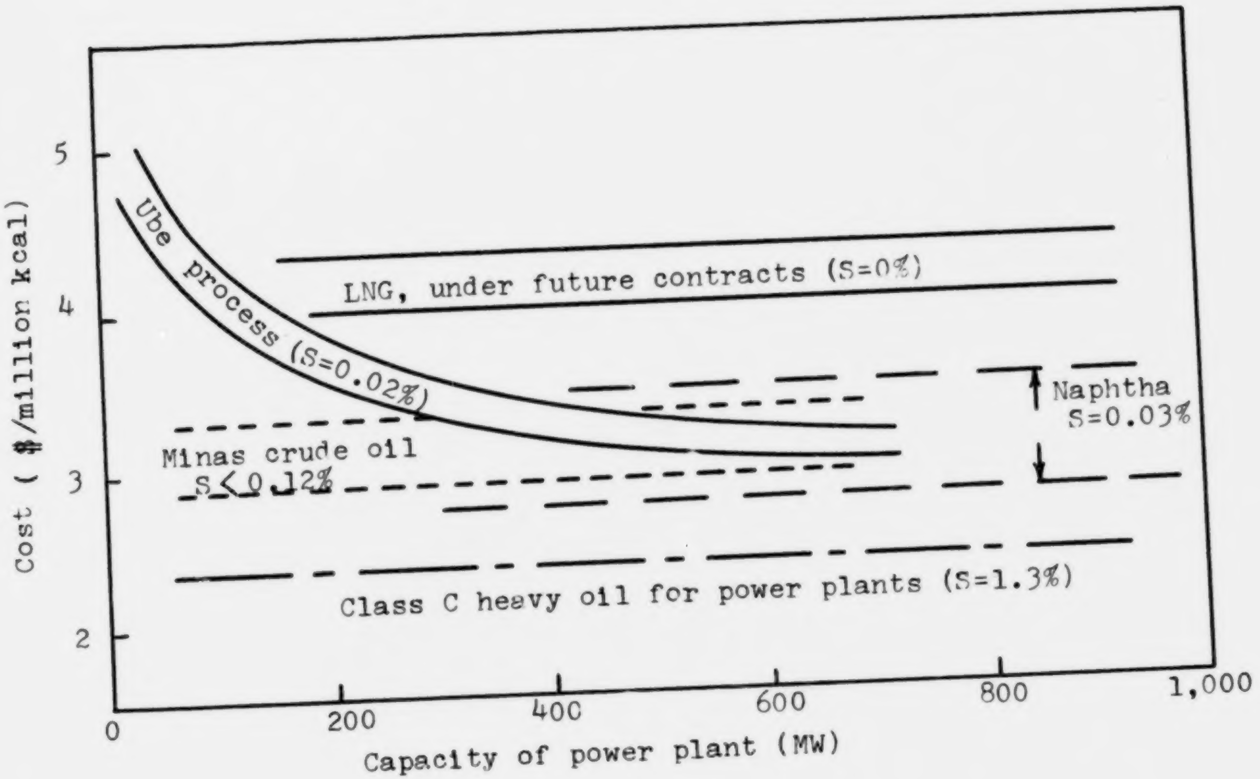


Figure 3.2.3 Cost and sulfur content of fuels for power plants

3.3 Other processes for gasification of heavy oil

3.3.1 Kureha process

Kureha Chemical Industries (1-8, Horidomecho, Nihonbashi, Chuo-ku, Tokyo) has recently operated a pilot plant to decompose residual oil from vacuum distillation 220 lb/hr at 1,600-2,200°F by means of high temperature gas or steam. The reaction is carried out very rapidly in 1/1,000-1/100 second to produce olefines (C_2H_4 and C_3H_6), fuel gas, and tar and pitch with special qualities. There is no plan yet to build a larger plant because good uses for the tar and pitch have not been found yet.

3.3.2 Japan Gasoline process

Japan Gasoline Co. (2-4, Otemachi, Chiyoda-ku, Tokyo) has been trying to develop a process for power generation by gasification desulfurization of heavy oil, as was described by the present author in his 1972 report. The process features the partial oxidation of heavy oil with air under pressure and also the use of gas and steam turbines for power generation. No notable progress has been made during the past year or so.

3.3.3 TEC process

Tokyo Engineering Co. (TEC, 2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo) has developed a new catalytic process to gasify heavy hydrocarbons. With the process, not only the distillates such as naphtha and gas oil, but also all kinds of hydrocarbon oils including crude oil, atmospheric residue and vacuum residue can be completely gasified by steam reforming reaction with almost no carbon deposit on the catalyst surface. The product of this process is a mixture of hydrogen, methane, CO and CO_2 which can be used as fuel gas. A joint development program has been launched to exploit the potentials of this process by TEC and Tokyo Gas Co.

4 Outline of waste-gas desulfurization

Major commercial and prototype plants in operation and under construction for SO_2 removal and recovery are listed in Tables 4.1 to 4.4. The tables show about 40 plants (70 units) in operation with a total capacity of about 5,000,000 scfm and several plants under construction. Nearly a half of the plants treat flue gas from oil-fired boilers and the rest waste gases from pulp plants, sulfuric acid plants, smelteries, iron ore sintering plants, Claus furnaces, etc. The unit capacity of most of the desulfurization plants ranges from 20,000 to 250,000scfm. There are many other smaller commercial plants treating waste gas from various sources which are not listed in the tables. The capacities of the desulfurization plants in operation total 6,000,000scfm.

Major electric power companies were interested in dry processes but have recently decided to build many large plants using wet processes as shown in Table 4.5. The capacities of the desulfurization plants of the major power companies will total 2,700MW in 1974, 3,700MW in 1975, and 4,800MW in 1976 (Table 1.6).

A salient feature of the desulfurization efforts in Japan is that they are oriented toward processes that yield salable by-products. Of the plants in operation about 60%, in terms of capacity, use sodium scrubbing to produce sodium sulfite and sulfate for paper mills (Table 4.1), 27% other recovery processes to produce concentrated SO_2, sulfuric acid and gypsum (Tables 4.2 and 4.3), and only 13% removal processes to produce waste by-products such as solid calcium sulfite and solutions of ammonium sulfate and sodium sulfite or sulfate (Table 4.4).

This is because Japan is subject to limitations in domestic supply of sulfur and its compounds as well as in land space available for disposal of useless by-products. The by-produced sodium sulfite, however, has already filled the demand. Most of the plants now planned (Table 4.5) as well as the pilot plants in operation (Table 4.6) aim at the production of salable gypsum or sulfuric acid. As desulfurization is making rapid progress, it will not be long before the supply of by-products runs ahead of demand.

Table 4.1 Major SO_2 recovery plants by sodium scrubbing (charge: NaOH)

Process developer	Product	User	Plant site	Unit capacity(1,000scfm)	Date of completion
Oji Paper	Na_2SO_3	Oji Paper	Kasugai	805(in 12 units)[a,b]	1966-1972
Oji Paper	Na_2SO_3	Tokai Pulp	Shimada	467(in 5 units)[b]	1970-1972
Oji Paper	Na_2SO_3	Daio Paper	Mishima	470(in 6 units)[b]	1972
Oji-Jinkoshi	Na_2SO_3	Oji Paper	Tomakomai	400(in 4 units)[a]	1971-1972
Kureha Chemical	Na_2SO_3	Kureha Chemical	Nishiki	176[a], 176[a]	1968
Kureha Chemical	Na_2SO_3	Mitsui Toatsu	Nagoya	112[a]	1971
Kureha Chemical	Na_2SO_3	Konan Utility	Konan	123[a]	1972
Showa Denko	Na_2SO_3	Showa Denko	Kawasaki	88[a]	1970
Showa Denko	Na_2SO_3	Ajinomoto	Kawasaki	159[a]	1971
Showa Denko	Na_2SO_3	Nippon Phosphoric	Sodegaura	47[c]	1971
Showa Denko	Na_2SO_3	Asia Oil	Yokohama	142[a]	1972
Tsukishima	Na_2SO_3	Sumitomo Mining	Toyo, Besshi	82[c], 88[d]	1970
Bahco-Tsukishima	Na_2SO_3	Daishowa Paper	Yoshinaga	129[b], 65[b], 26[b]	1971
Bahco-Tsukishima	Na_2SO_3	Daio Paper	Iyomishima	88[a], 70[a]	1972
Cadelius	Na_2SO_3	Hokuetsu Paper	Niigata	100[b], 100[b]	1971
Cadelius	Na_2SO_3	Sanyo Kokusaku Pulp	Asahikawa	77[b]	1972
Hitachi Ltd.	Na_2SO_3	Jujo Paper	Miyakojima	57[a]	1972
Ishikawajima-TCA	Na_2SO_4	Tsurumi Soda	Yokohama	35[a]	1971
Ishikawajima-TCA	Na_2SO_4	Mitsuisenpoku Oil	Sakai	88[a], 88[a], 88[a]	1973
Mitsubishi(MKK)	Na_2SO_4	Asahi Glass	Amagasaki	41[e]	1972
Mitsubishi(MKK)	Na_2SO_4	Asahi Glass	Tsurumi	130[e]	1973

a: Oil-burning boiler   b: Kraft recovery boiler   c: H_2SO_4 plant

d: Smelting furnace   e: Glass furnace

Table 4.2 SO_2 recovery plants by wet process to produce gypsum

Process developer	Absorbent	User	Plant site	Unit capacity (1,000scfm)	Date of completion
Mitsubishi-JECCO	$Ca(OH)_2$	Nippon Kokan	Koyasu	37[c]	1968
Mitsubishi-JECCO	$Ca(OH)_2$	Kansai Electric	Amagasaki	59[a]	1972
Mitsubishi-JECCO	$Ca(OH)_2$	Onahama S. & R.	Onahama	54[d]	1972
Mitsubishi-JECCO	$Ca(OH)_2$	Tomakomai Chem.	Tomakomai	35[d]	1972
Mitsubishi-JECCO	$Ca(OH)_2$	Kawasaki Steel	Chiba	71[g]	1973
Bahco-Tsukishima	$Ca(OH)_2$	Yahagi Iron	Nagoya	47[g]	1971
Ishikawajima-TCA	$Ca(OH)_2$	Mitsubishi Metal	Onahama	70[d]	1972
Ishikawajima-TCA	$Ca(OH)_2$	Chichibu Cement	Kumagaya	61[h]	1972
Ishikawajima-TCA	$Ca(OH)_2$	Chichibu Cement	Kumagaya	61[h]	1973
Kawasaki H.I.	$Ca(OH)_2$	Jujo Paper	Akita	53[b]	1973
Chiyoda	H_2SO_4, $CaCO_3$	Nippon Mining	Mizushima	20[f]	1972
Chiyoda	H_2SO_4, $CaCO_3$	Fuji Kosan	Kainan	93[a]	1972
Chiyoda	H_2SO_4, $CaCO_3$	Mitsubishi Rayon	Otake	53[a]	1973
Chiyoda	H_2SO_4, $CaCO_3$	Tohoku Oil	Sendai	8[f]	1973
Chiyoda	H_2SO_4, $CaCO_3$	Daicel Ltd.	Aboshi	59[a]	1973
Nippon Kokan	NH_3, $Ca(OH)_2$	Nippon Kokan	Keihin	88[g]	1972
Nippon Steel Chem.	NaOH, $Ca(OH)_2$	Nippon Steel Chem.	Sakai	12[d]	1972
Showa Denko	NaOH, $CaCO_3$	Showa Denko	Chiba	340[a]	1973

---

a: Oil-burning boiler
b: Kraft recovery boiler
c: Sulfuric acid plant
d: Smelting furnace
f: Claus furnace
g: Sintering plant
h: Diesel generator

Table 4.3 Other major plants for SO_2 recovery

Process developer	Absorbent	Product	User	Plant site	Unit capacity (1,000scfm)	Date of completion
Wet process						
Wellman-Lord(MKK)	NaOH	SO_2, H_2SO_4	Japan Synth. Rubber	Chiba	118^a	1971
Wellman-Lord(MKK)	NaOH	SO_2, H_2SO_4	Chubu Electric	Nishinagoya	365^a	1973
Wellman-Lord(MKK)	NaOH	SO_2, H_2SO_4	Nihon Synth. Rubber	Yokkaichi	237^a	1973
Wellman-Lord(SCEC)	NaOH	SO_2, S	Toa Nenryo	Kawasaki	35^f	1971
Wellman-Lord(SCEC)	NaOH	SO_2, H_2SO_4	Sumitomo Chiba Chem.	Chiba	212^a	1973
Mitsui Min. & Sm.	MgO	SO_2, H_2SO_4	Mitsui Min. & Sm.	Hibi	47^c	1971
Cnahama-Tsukishima	MgO	SO_2, H_2SO_4	Onahama Smelt.	Onahama	53^d	1972
Mitsubishi-IFP	NH_4OH	SO_2, S	Maruzen Oil	Wakayama	24^f	1974
Dry process						
Sumitomo S.M.	Carbon	SO_2, H_2SO_4	Kansai Electric	Sakai	100^a	1971
Mitsubishi H. I.	MnO_x, NH_3	$(NH_4)_2SO_4$	Chubu Electric	Yokkaichi	193^a	1972
Hitachi Ltd.	Carbon $CaCO_3$	H_2SO_4 Gypsum	Tokyo Electric	Kashima	250^a	1972
Shell	CuO	SO_2, S	Showa Y. S.	Yokkaichi	71^a	1973

a: Oil-burning boiler c: Sulfuric acid plant

d: Smelting furnace f: Claus furnace

Table 4.4 Major plants for SO_2 removal (waste product)

Process developer	Absorbent	Product	User	Plant site	Unit capacity (1,000scfm)	Year of completion
Kurabo Ind.	Waste NaOH	Na_2SO_4	Kurabo Ind.	Hirakata	32[a]	1970
Kurabo Ind.	NH_3	$(NH_4)_2SO_4$	Mitsubishi Elec. Co.	Amagasaki	24[a]	1971
Kurabo Ind.	NH_3	$(NH_4)_2SO_4$	Ishigasome Sarashi	Tokyo	14[a]	1971
Kurabo Ind.	NaOH	Na_2SO_4	Bridgestone Tire	Tokyo, Nasu	71[a], 28[a]	1972
Kurabo Ind.	NaOH	Na_2SO_4	Rengo	Ibaraki	30[a]	1972
Kurabo Ind.	NaOH	Na_2SO_4	Kanzaki Paper	Amagasaki	24[a], 24[a]	1972
Mitsubishi H.I.	NaOH	Na_2SO_3	Morinaga Milk	Tama	31[a]	1972
Toyobo Co.	Waste NaOH	Na_2SO_3	Toyobo Co.	Moriguchi	26[a]	1970
Toyobo Co.	Waste NaOH	Na_2SO_3	Toyobo Co.	Shogawa	24[a]	1971
Kawasaki H.I.	NaOH	Na_2SO_4	Sumitomo Rubber	Kobe	17[a]	1972
Bahco-Tsukishima	NaOH	Na_2SO_3	City of Tokyo	Odai	110[i]	1972
Ishikawajima-TCA	NaOH	Na_2SO_4	Hokushin Goban	Osaka	26[a]	1971
Ishikawajima-TCA	NaOH	Na_2SO_4	Eidai Sangyo	Osaka	24[a]	1972
Ishikawajima-TCA	NaOH	Na_2SO_4	Nissan Motor	Oppama	67[a]	1972
Chemico Mitsui	$Ca(OH)_2$	$CaSO_3$	Mitsui Aluminum	Omuta	226[j]	1972

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a: Oil-fired boiler

i: Burning of sludge from sewage treatment plants

j: Coal-fired boiler

Table 4.5 Flue-gas desulfurization plants of major power companies to be completed in 1973 and 1974 (Oil-fired boiler)

Power company	Plant site	Capacity(MW)	Process developer	Absorbent	Product
Tokyo Electric	Yokosuka	130	Mitsubishi-JECCO	$CaCO_3$	Gypsum
Tohoku Electric	Hachinoe	125	Mitsubishi-JECCO	$Ca(OH)_2$	Gypsum
Tohoku Electric	Shinsendai	150	Kureha-Kawasaki	$NaOH$, $CaCO_3$	Gypsum
Chubu Electric	Nishinagoya	220	Wellman-Lord(MKK)	$NaOH$	SO_2 H_2SO_4
Kansai Electric	Amagasaki	125	Mitsubishi-JECCO	$Ca(OH)_2$	Gypsum
Kansai Electric	Kainan	150	Mitsubishi-JECCO	$Ca(OH)_2$	Gypsum
Chugoku Electric	Mizushima	100	Babcock-Hitachi	$CaCO_3$	Gypsum
Shikoku Electric	Shintokushima	150	Kureha-Kawasaki	$NaOH$, $CaCO_3$	Gypsum
Hokuriku Electric	Shinminato	250	Chiyoda	H_2SO_4, $CaCO_3$	Gypsum

Table 4.6 Major pilot plants for SO_2 recovery

Process developer	Absorbent	Product	Plant site	Unit capacity(scfm)
Wet process				
Grillo-Mitsui S. B.	MgO, MnO	SO_2, H_2SO_4	Chiba	710
Kawasaki H.I.	$Ca(OH)_2$	Gypsum	Kakogawa	2,900
Mitsui M.B.-Chemico	$CaCO_3$	Gypsum	Omuta	1,200
Hitachi S.B.	NaClO, $CaCO_3$	Gypsum	Maizuru	290
Kureha-Kawasaki	NaOH, $CaCO_3$	Gypsum	Nishiki	2,900
Showa Denko	NaOH, $CaCO_3$	Gypsum	Kawasaki	5,900
Babcock-Hitachi	$CaCO_3$	Gypsum	Kure	1,800
Kurashiki Boseki	NH_3, $Ca(OH)_2$	Gypsum	Hirakata	5,900
Furukawa Mining	NH_3, $Ca(OH)_2$	Gypsum	Osaka	350
Hitachi Ltd.	NaOH, $Ca(OH)_2$	Gypsum		880
Nippon Kokan	$Ca(OH)_2$	Gypsum	Koyasu	1,200
Dry process				
National R.I.P.R.	Na_2CO_3	SO_2, S	Kawaguchi	120
Sumitomo S.M.	Carbon	H_2SO_4		5,900

5 Wet-alkali and double alkali processes

5.1 Kureha sodium-limestone process[7, 8]

Developer Kureha Chemical Industry Co.
1-8, Horidomecho, Nihonbashi, Chuo-ku, Tokyo

State of development Kureha first developed a sodium scrubbing process to produce solid sodium sulfite to be sold to paper mills as was described in the 1972 report of the present author. In addition to two 176,000scfm plants operated by Kureha since 1969, two plants have been licensed, one to Mitsui Toatsu Chemical (112,000scfm) which began operation in September 1971, and the other to Konan Utility (123,000scfm) which started operation in late 1972. Since the demand for sodium sulfite is limited, Kureha has recently developed a sodium-calcium double-alkali process. Tests with a small pilot plant led to the construction of a larger pilot plant (3,000scfm) which has been in operation since July 1972. The larger pilot plant program is a joint effort with Kawasaki Heavy Industries. Two commercial plants will be completed in 1974 to treat flue gas from oil-fired boilers at power companies, one at Shinsendai station, Tohoku Electric Power (150MW), and the other at Shintokushima station, Shikoku Electric Power (150MW).

Process description A flow sheet of the sodium-calcium process is shown in Figure 5.1. The scrubbing system consists of a venturi scrubber where water is used to remove particulates and to cool the gas followed by a rubber-lined, grid-packed scrubber where SO_2 is absorbed in a sodium sulfite solution. The water from the dust scrubber is discharged at a pH of about 2.5. The pH of the liquor from the absorber is controlled to 6.0-6.5. With an inlet concentration of 1,500ppm SO_2, 98% removal is achieved; the liquid gas ratio is 7gal/1,000ft^3 of gas. The feed to the absorber contains 20-25% sodium sulfite and has a pH of 7-8; the calcium content was reported to be about 30ppm. The scrubber discharge contains about 10% sodium sulfite, 10% sodium bisulfite, and 2-5% sodium sulfate. Limestone pulverized in a wet mill equipped with a cyclone classifier is fed continuously along with scrubber liquor into an atmospheric pressure vessel where sodium bisulfite reacts with limestone to form calcium and sodium sulfites.

$$2NaHSO_3 + CaCO_3 \longrightarrow CaSO_3\cdot 1/2H_2O + Na_2SO_3 + 1/2H_2O + CO_2$$

The reaction temperature is somewhat higher than the scrubber temperature which is about 140°F; residence time for conversion is about 2 hours. The slurry from the decomposer is passed through a centrifuge where the calcium sulfite crystals are separated from sodium sulfite liquor, which is then returned to the scrubber.

The calcium sulfite is reacted with air at atmospheric pressure in an oxidizer developed by Kureha. Gypsum is removed from the oxidizer discharge stream by a centrifuge. The product is suitable for use in wallboard and cement.

Oxidation of sulfite in the scrubbing and decomposition steps results in the formation of sodium sulfate which cannot be regenerated by reaction with limestone. In order to control the sulfate level, a sidestream from the scrubber discharge is mixed with calcium sulfite crystals and sulfuric acid is added. The net effect is to convert the sodium sulfate to calcium sulfate and produce sodium bisulfite for recycle. Gypsum is separated by a centrifuge and added to the oxidizer loop.

$$H_2SO_4 + CaSO_3 \cdot 1/2H_2O + 1/2H_2O \longrightarrow SO_2 + CaSO_4 \cdot 2H_2O$$

$$SO_2 + CaSO_3 \cdot 1/2H_2O + Na_2SO_4 + 5/2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaHSO_3$$

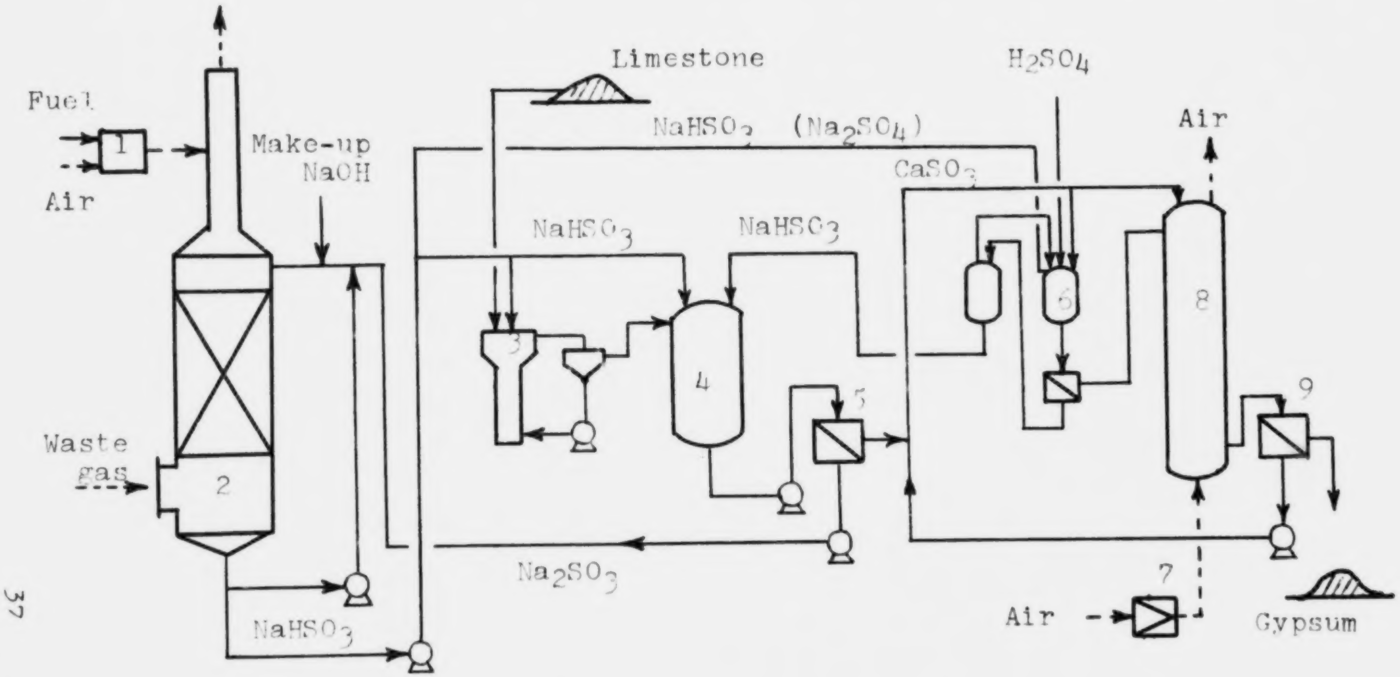
Status of pilot plant operation The pilot plant (3,000scfm) has been operated continuously since its completion in July 1972 except for the scheduled shutdown for inspection in September and December. Almost no scaling was observed. Operation of the centrifuges has given effective separation of solid and liquid phases. Both calcium sulfite and gypsum discharged from the centrifuge are dump solids which can be transported by solid-handling equipment, if desired. The crystals of gypsum grow to around 100 microns. The flue gas contains about 6% oxygen. About 7% of the recovered SO_2 is oxidized to form sodium sulfate. The sulfuric acid requirement for the decomposition of the sulfate is 125% of the theoretical amount. Therefore, about 8.7% of the product gypsum is derived from sulfuric acid.

Economics For the production of a ton of gypsum, 1,200 lb of limestone, 18 lb of caustic soda (100%) for make-up, 100 lb of sulfuric acid (98%), 340kWh of electric power, 1,460 lb of steam, and 18 tons of water are required. Investment cost is uncertain, but the investment requirement would be split among the process steps as follows:

Absorption 30%, Decomposition 30%, Sulfate conversion 10%, Oxidation 30%.

Advantages High recovery of SO_2 is achieved with limestone. No scaling. Sodium sulfate is decomposed to recover sodium bisulfite and gypsum. Good quality of salable gypsum is obtained. Both gypsum and calcium sulfite discharged from the centrifuge have less moisture and are easy to handle.

Disadvantages The process is less simple than the lime-gypsum process. The use of a considerable amount of sulfuric acid it disadvantageous for plants where the product calcium sulfite or gypsum must be discarded.


Fuel
Air
1
Make-up NaOH
Waste gas
2
Limestone
$NaHSO_3$ (Na_2SO_4)
H_2SO_4
Air
$CaSO_3$
$NaHSO_3$
$NaHSO_3$
3
4
5
6
8
9
7
Na_2SO_3
$NaHSO_3$
Air
Gypsum

(1) Reheater (2) Absorber (3) Mill and classifier
(4) Decomposition tank (5) Centrifuge (6) Sulfate conversion tank
(7) Air compressor (8) Oxidizer (9) Centrifuge

Figure 5.1 Flow sheet of Kureha sodium-limestone process

5.2 Showa Denko sodium-limestone process[7, 8]

Developer Showa Denko K.K.
34, Shiba Miyamotocho, Minato-ku, Tokyo

Ebara Manufacturing Co. Ltd.
11-1, Asahimachi, Haneda, Ota-ku, Tokyo

State of development Showa Denko, jointly with Ebara, recently constructed commercial plants for SO_2 recovery by sodium scrubbing to produce sodium sulfite for paper mills. The plants include Kawasaki plant (88,000scfm) of Showa Denko, Kawasaki plant (159,000scfm) of Ajinomoto, and Yokohama plant (142,000scfm) of Asia Oil for flue gas from oil-fired boilers, and Sodegaura plant (47,000scfm) of Nippon Phosphoric Acid to treat tail gas from a sulfuric acid plant. As demand for sodium sulfite is limited, Showa Denko and Ebara have started joint tests on sodium-calcium process to by-produce salable gypsum. A pilot plant (5,900scfm) has been in operation at Kawasaki plant of Showa Denko since 1971. A commercial plant to treat 340,000scfm of flue gas is being constructed at Chiba plant, Showa Denko, to start operation in June 1973.

Process description The Showa Denko-Ebara process features the use of a vertical-cone type absorber as shown in Figures 5.2.1 and 5.2.4. A liquid (sodium sulfite solution) is charged from the bottom, blown up by the gas to absorb SO_2, and flows back to the liquor inlet by gravity. Very good contact between gas and liquid particles is attained ensuring 95-98% desulfurization at a liquid/gas ratio of 7-14 gal./1,000scf (Figure 5.2.2). Pressure drop ranges from 8 to 15 in.H_2O. A flow sheet of the sodium-calcium process is shown in Figure 5.2.3. Flue gas from an oil-fired boiler containing 1,500ppm SO_2 and about 1 grain/cf dust is led directly into the scrubber; 95% of the SO_2 and about 60% of the dust is removed by a sodium sulfite solution. Most of the liquor discharged from the scrubber is recycled to the scrubber. A portion of the liquor is led to a reactor and treated with pulverized limestone.

$$2NaHSO_3 + CaCO_3 = Na_2SO_3 + CaSO_3 + H_2O + CO_2$$

The calcium sulfite is separated from the sodium sulfate solution; the solution is returned to the scrubber. Calcium sulfite is oxidized in an oxidizer to form gypsum. As sodium sulfate gradually forms in the solution and tends to accumulate, a portion of the liquor discharged from the scrubber is sent to a sulfate conversion step to maintain the sulfate concentration at a certain level. In the conversion step, the sulfate is treated with calcium sulfite and sulfuric acid to produce gypsum and sodium bisulfite.

$$Na_2SO_4 + 2CaSO_3 + H_2SO_4 + 2H_2O = 2(CaSO_4 \cdot 2H_2O) + 2NaHSO_3$$

The bisulfite solution is led to the reactor.

Status of technology The pilot plant has been operated for more than one year without serious trouble. Both lime and limestone have been used for comparison. Limestone reacts slowly with sodium bisulfite requiring a few hours. By using lime the reaction proceeds rapidly. However, limestone will be used in the commercial plant because it is much cheaper than lime, and moreover, larger crystals of gypsum is obtained with limestone. An oxidizer developed by Showa Denko and Ebara will be used in the commercial plant. The oxidation proceeds a little more slowly but the crystals of gypsum grow larger than with a rotary atomizer developed by JECCO.

Advantages The scrubber is very effective for desulfurization. High recovery of SO_2 is achieved consuming limestone.

Disadvantages The process is less simple than the lime-gypsum process. The use of a considerable amount of sulfuric acid is a demerit for plants whose by-product gypsum or calcium sulfite must be discarded.

Economics The estimated desulfurization cost for a 120,000scfm plant for 95% removal of SO_2 is shown below.

Plant cost $1.7 million
7,000 hours operation in a year
By-product gypsum 192,000 tons/year

Requirements (lb per bl oil)					
NaOH	H_2SO_4	CaO	Water	Steam	Electricity
0.56	5.0	35.8	560	0.38	10(kWh)

Variable cost	$0.331/bl oil
Fixed cost	$0.687/bl oil
Desulfurization cost	$1.018/bl oil (without credit for gypsum) $0.936/bl oil (with credit for gypsum)

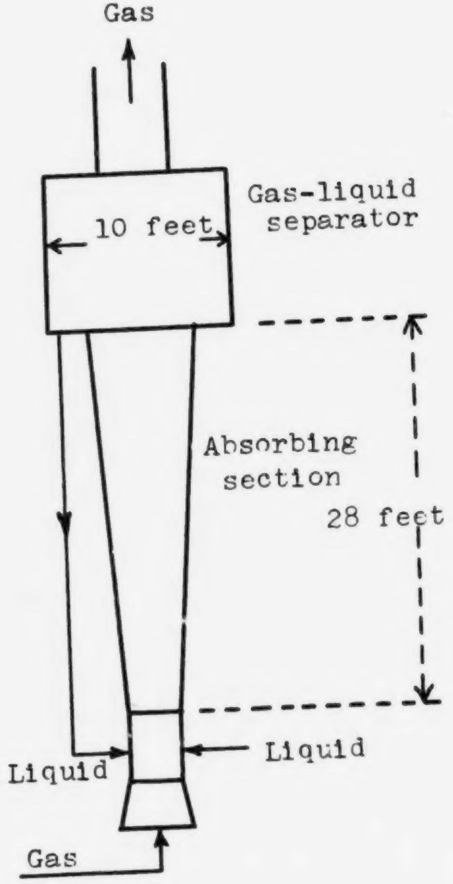

Gas
Gas-liquid separator
10 feet
Absorbing section
28 feet
Liquid
Liquid
Gas

Figure 5.2.1 Vertical-cone type absorber for 60,000acfm

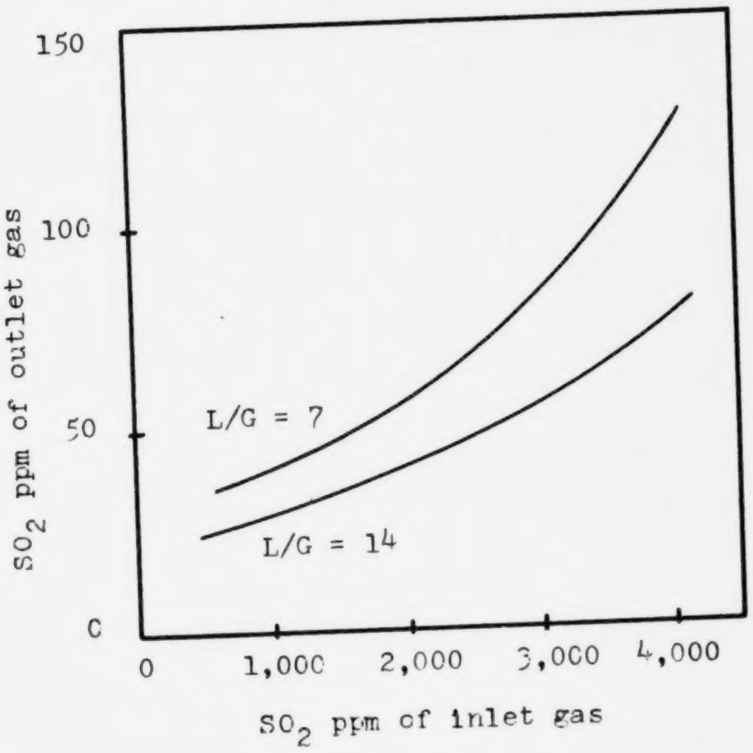


Figure 5.2.2 Relation between liquid/gas ratio (gal./1,000scf) and SO_2 removal (pH 6.5)

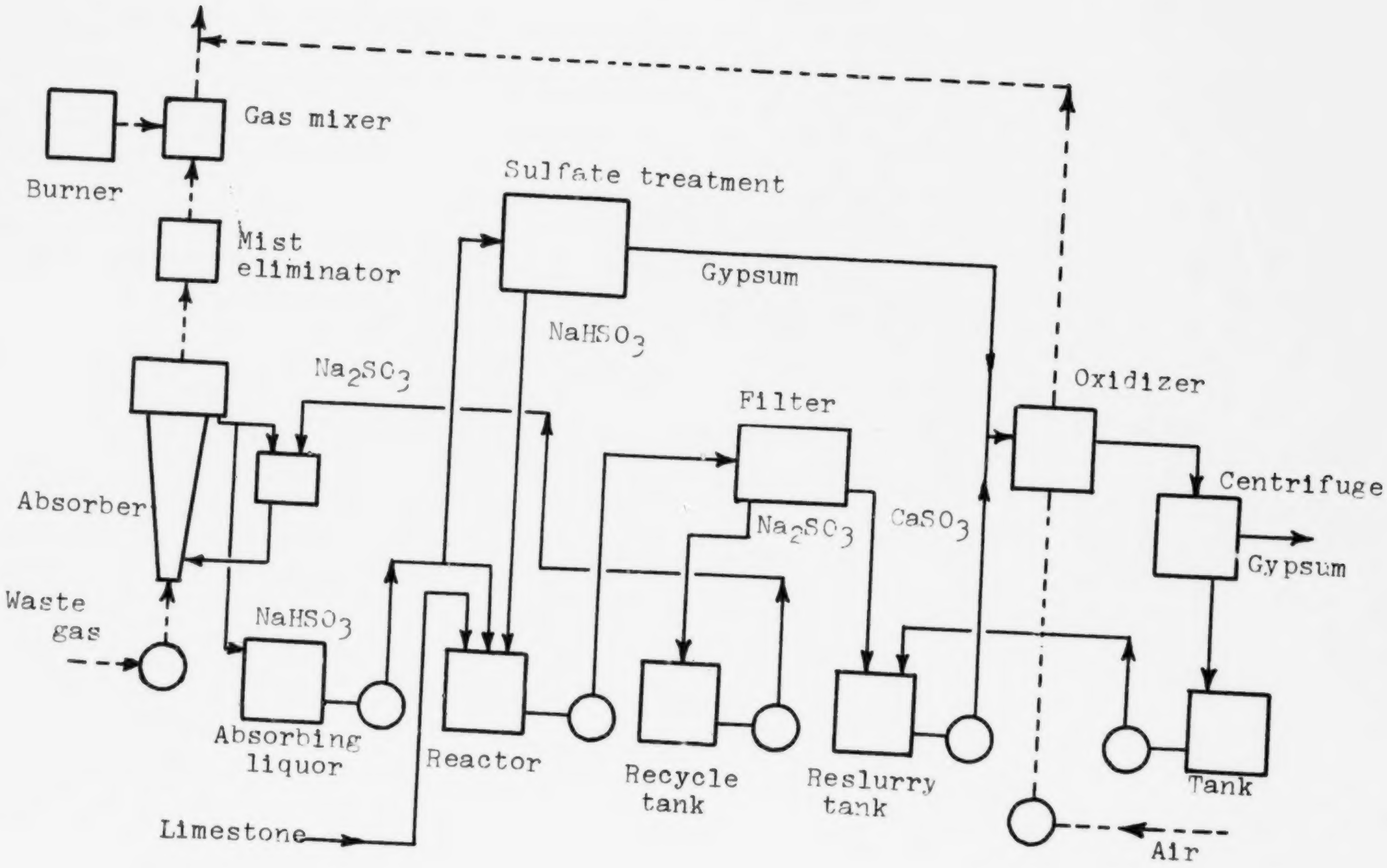

Gas mixer
Burner
Sulfate treatment
Mist eliminator
Gypsum
NaHSO$_3$
Na$_2$SO$_3$
Filter
Oxidizer
Absorber
Centrifuge
Na$_2$SO$_3$
CaSO$_3$
Gypsum
Waste gas
NaHSO$_3$
Absorbing liquor
Reactor
Recycle tank
Reslurry tank
Tank
Limestone
Air

Figure 5.2.3 Showa Denko sodium-limestone process

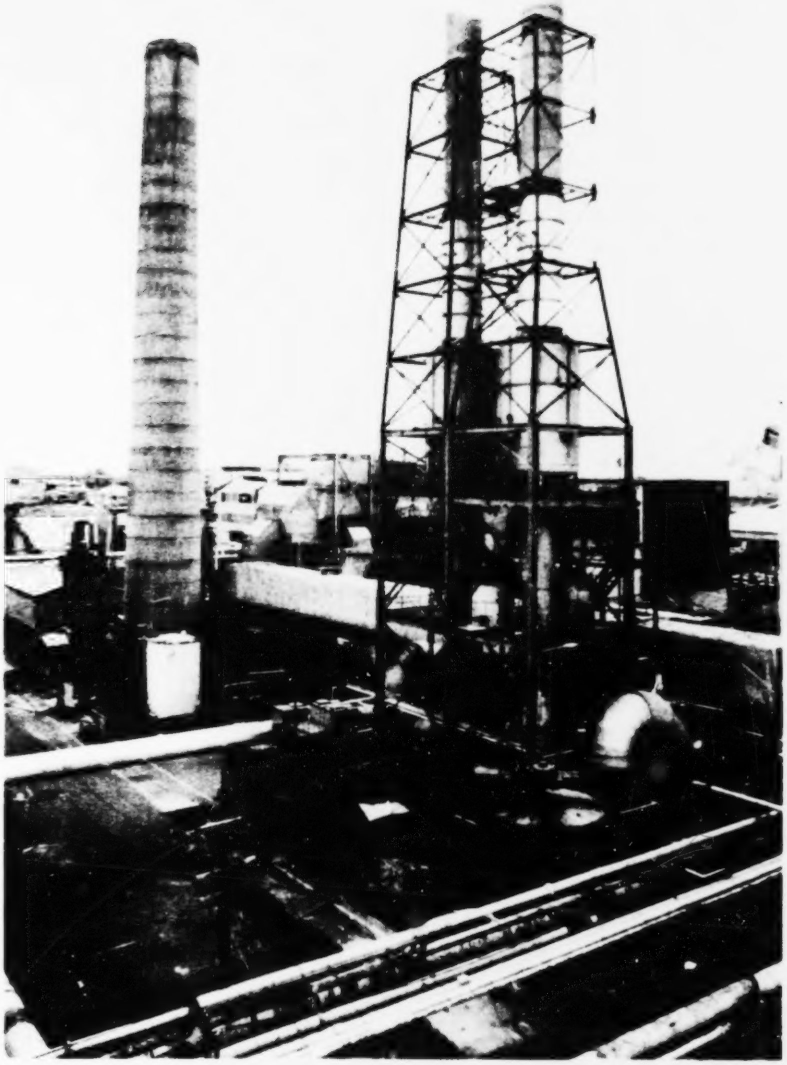


Figure 5.2.4 Kawasaki plant of Showa Denko
(sodium scrubbing, 88,000scfm)

5.3 Hitachi sodium process and sodium-lime process 7)

Developer Hitachi Ltd.
2-8, Otemachi, Chiyoda-ku, Tokyo

5.3.1 Semi-wet sodium process

Process description Flue gas from oil-fired boiler at about 350°F after passing through a dust eliminator is introduced into a reactor into which sodium hydroxide solution is fed and mixed with the gas by a mixer (Figure 5.3.1). By the heat of the gas, moisture is removed and a powdery product consisting of sodium sulfite, sulfate and carbonate (for example Na_2SO_3 60%, Na_2SO_4 20%, and Na_2CO_3 20%) is formed which is caught by a multiclone, electrostatic precipitator, or bag filter. The product is usable for kraft pulp production. The temperature of the outlet gas from the dust eliminators is kept above 210°F. The SO_2 concentration of the inlet gas is about 1,300ppm and that of the outlet gas 100 to 150ppm. The dust content of the outlet gas to stack is 0.02-1 grain/scf and is below the emission standard. The size of the reactors for different amounts of gas is shown below:

Amount of gas (scfm)	Size of reactor (feet)	
	Diameter	Height
11,800	7.9	62.7
30,000	9.6	82.5
59,000	14.8	92.4

State of development Two commercial plants of Jujo Paper Co. are in operation; one was completed at Jujo plant (16,500scfm) in August 1971 and the other at Miyakojima plant (57,000scfm) in October 1972.

Advantages The process is very simple. Reheating of the gas is not required when the temperature of the inlet gas is higher than 300°F. Pressure drop is relatively small. No wastewater.

Disadvantage CO_2 in the gas is also absorbed consuming caustic soda. Use of the product is limited.

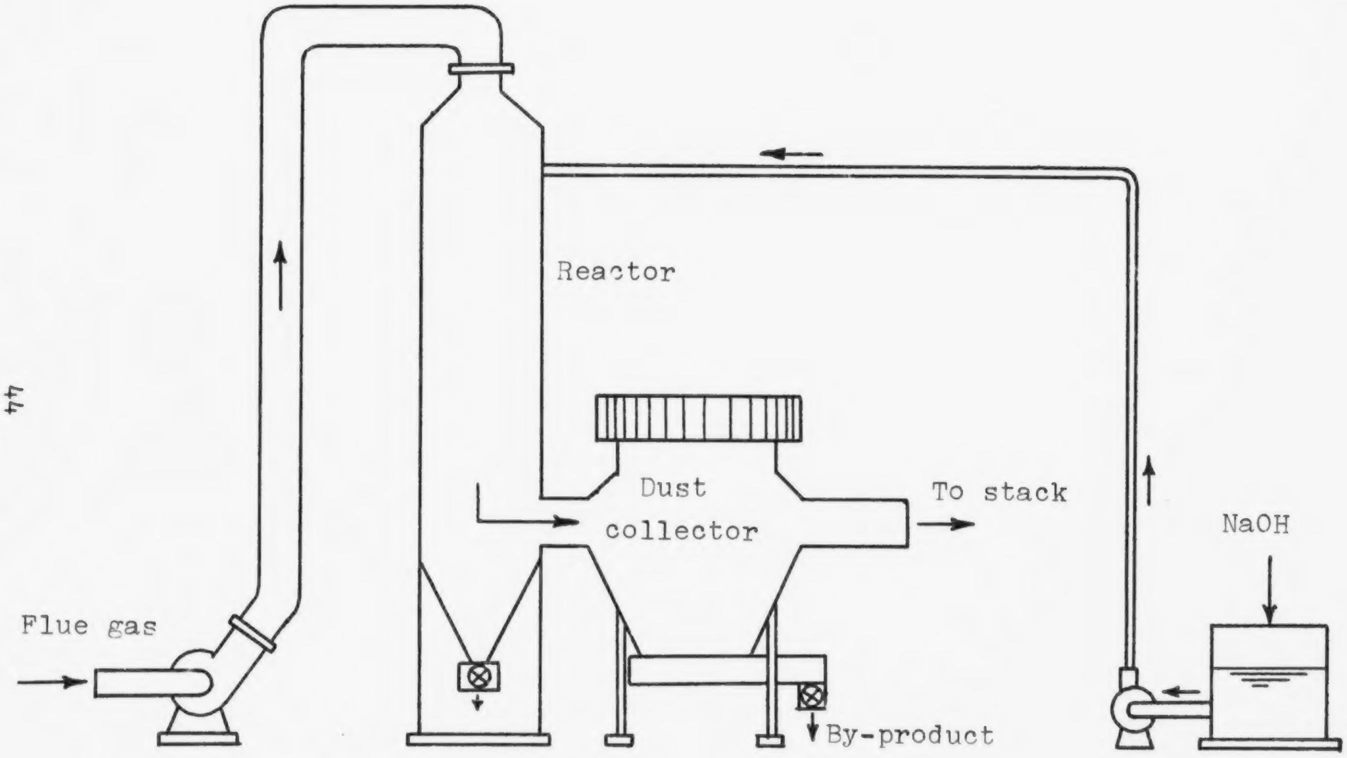

Flue gas
Reactor
Dust collector
To stack
By-product
NaOH

Figure 5.3.1 Hitachi semi-wet sodium process

5.3.2. Sodium scrubbing (sodium sulfate production)

Process description Flue gas is first led into a cooler to which a portion of an absorbing liquor is fed for cooling, partial desulfurization, and dust removal (Figure 5.3.2). The gas is then led into a dual-flow tray scrubber which has multistage horizontal plates with many holes about a half inch in diameter. Absorbing liquor (sodium sulfite solution) goes down from the top stage to the bottom through the holes while the gas goes up from the bottom through the holes forming numerous bubbles. The reacted liquor containing sodium bisulfite is neutralized with sodium hydroxide to regenerate the sulfite and is then returned to the scrubber. A portion of the sodium sulfite solution is led into an oxidizer to oxidize the sulfite into sulfate by introducing air bubbles. The sulfate solution is filtered for dust removal and put into the wastewater system. The size of the scrubber to reduce the SO_2 content from 1,000 to 100ppm and dust from 20 to 2mg/scf is shown below.

Amount of gas (scfm)	Size of scrubber (feet)	
	Diameter	Height
11,800	7.2	24.1
35,000	12.9	28.7
58,000	16.5	33.0
88,000	19.8	36.3

State of development Two commercial plants with capacities 14,000scfm and 35,000scfm have been in operation since August 1972.

Advantages The dual-flow tray scrubber is effective for removal of both SO_2 and dust. The process is simple and operation is easy.

Disadvantages Caustic soda is fairly expensive. Emission of a large amount of sodium sulfate might constitute a limiting factor in future.

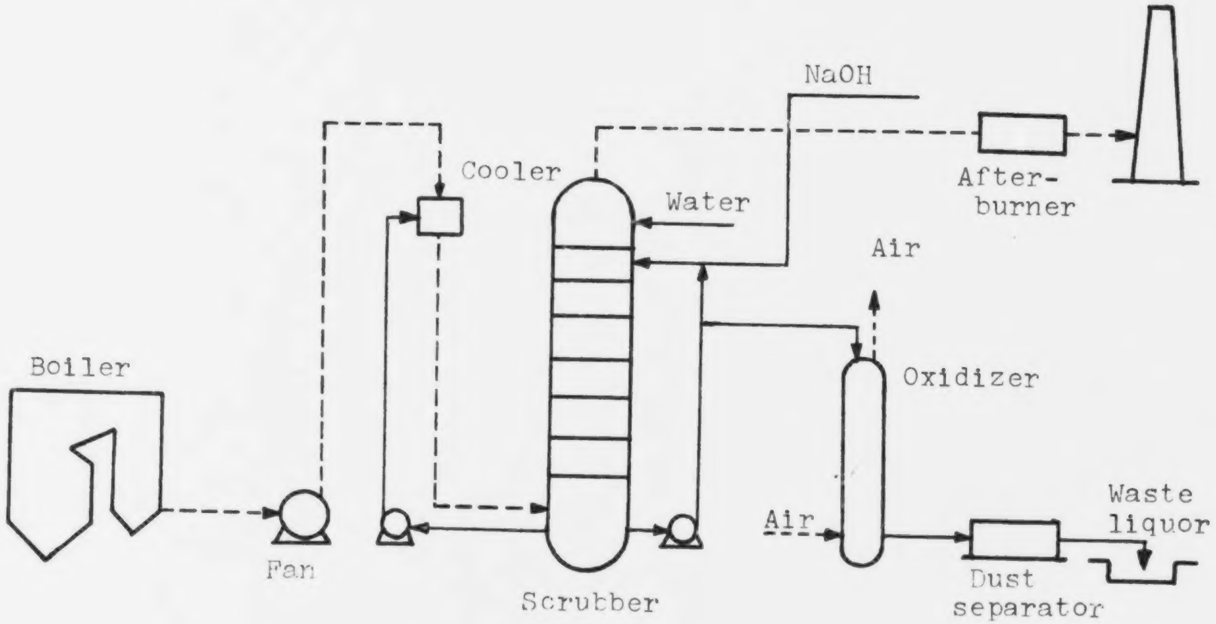

NaOH
Cooler
Water
After-
burner
Air
Boiler
Oxidizer
Waste
liquor
Air
Fan
Scrubber
Dust
separator

Figure 5.3.2 Hitachi sodium sulfate process (waste product)

5.3.3 Sodium-calcium process

Process description A flow sheet of the process is shown in Figure 5.3.3. The absorbing system is similar to that described in 5.3.2. A portion of the circulating solution containing sodium sulfite with some sulfate is reacted with milk of lime in a reactor to produce a slurry consisting of sodium hydroxide solution and solid calcium sulfite with some gypsum. The solids are separated from the solution by a thickener and a centrifuge; the solution is returned to the absorbing step and the solids are fed into an oxidizer where calcium sulfite is oxidized by air bubbles to produce salable gypsum. Sulfuric acid is used for pH adjustment of the slurry in the oxidizer. Hitachi has found an optimum condition for the conversion of sodium sulfate to gypsum.

State of development A pilot plant with a capacity of treating flue gas (880scfm) from an oil-fired boiler has been in operation.

Economics The requirements and products for 90% removal of SO_2 (1,500ppm) of flue gas is as follows:

	Amount of gas treated (scfm)			
	11,800	29,400	58,800	88,200
Requirements				
$Ca(OH)_2$ (lbs/hr)	176	429	858	1,287
Water (tons/hr)	1.3	3.3	6.6	9.9
Electric power (kW)	120	250	460	660
Steam (lbs/hr)	154	418	836	1,254
Products				
Gypsum (lbs/hr)	440	1,078	2,156	3,234

Some make-up canstic soda is also required. The desulfurization cost including depreciation (7 years) and assuming 8,000 hours operation in a year is estimated to be about $1,14/bl for 29,400scfm, $0.94/bl for 58,800scfm, and $0.73/bl for 117,600scfm.

Advantages High recovery of SO_2 is achieved and salable gypsum is by-produced without scaling problems. Essentially no wastewater is emitted.

Disadvantages The process is less simple than the lime-gypsum process. Sulfuric acid is required.

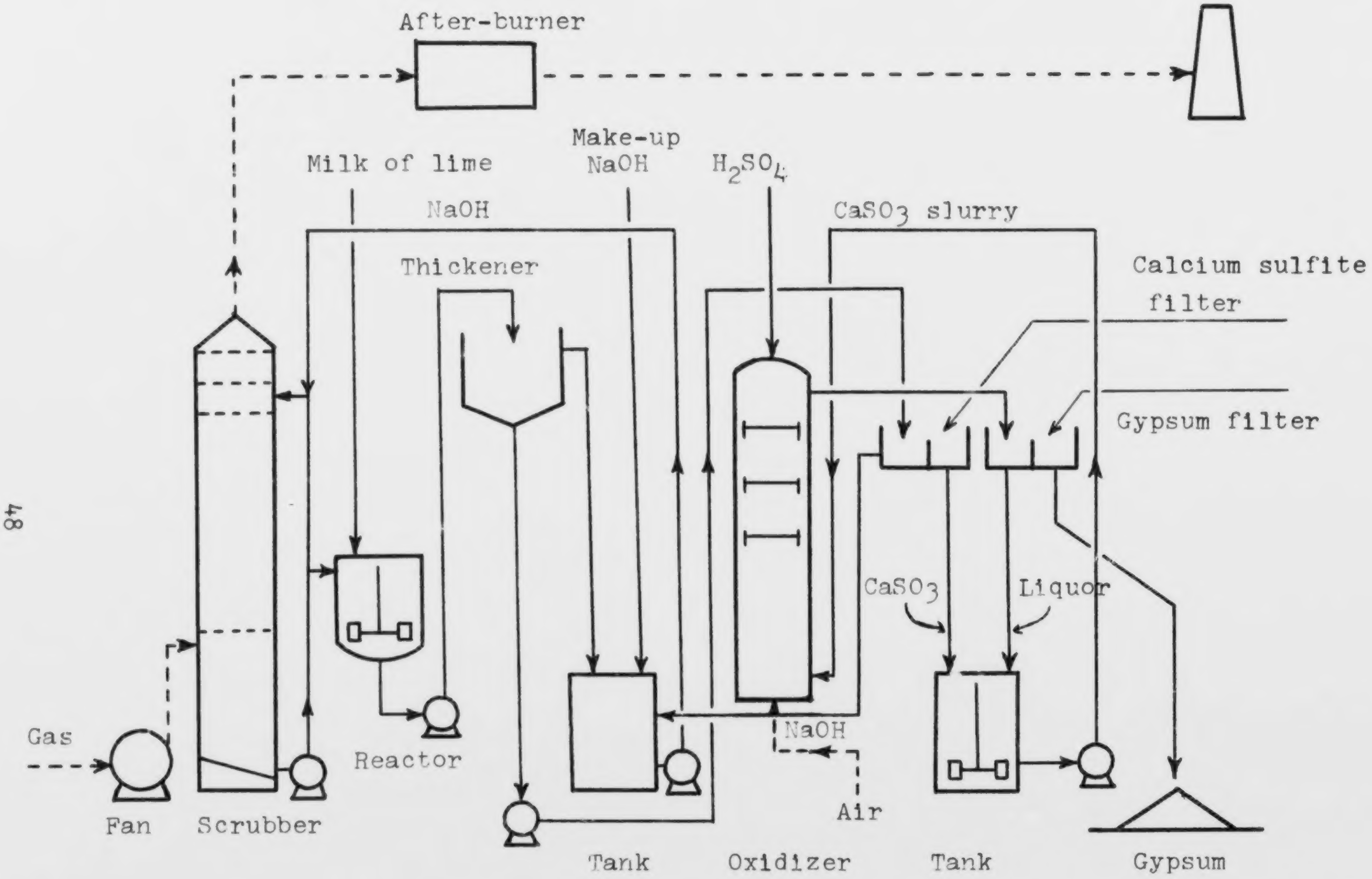

After-burner
Milk of lime
Make-up NaOH
H_2SO_4
NaOH
$CaSO_3$ slurry
Thickener
Calcium sulfite filter
Gypsum filter
$CaSO_3$
Liquor
Gas
NaOH
Air
Fan
Scrubber
Reactor
Tank
Oxidizer
Tank
Gypsum

Figure 5.3.3 Flow sheet of Hitachi sodium-lime process

5.4 Nippon Steel Chemical Sodium-lime process

Developer Nippon Steel Chemical Co. Ltd.
17-2, 6-chome, Ginza, Chuo-ku, Tokyo

Process description SO_2 in waste gas is absorbed by a sodium sulfite solution in two two-stage venturi type scrubbers in series developed by Miura Kagaku Sochi Co.(Figure 5.4). The liquor discharged from the scrubber normally contains about 10% sodium sulfite and bisulfite and about 5% sodium sulfate. A large portion of the liquor is neutralized with a sodium hydroxide solution and recycled to the scrubbers. The rest of the liquor is reacted with milk of lime (5% in excess) to precipitate calcium sulfite with some sulfate and to form a sodium hydroxide solution. The slurry is sent to a thickener. The concentrated slurry from the bottom of the thickener is fed to a vacuum filter. The filtered cake contains 50 to 60% moisture. The filtrate and the overflow from the thickener (sodium hydroxide solution) is used along with make-up sodium hydroxide to neutralize the liquor discharged from the scrubber. The desulfurization ratio reaches 96 to 98%. The sodium sulfate concentration in the circulating liquor gradually increases until it reaches about 10% but it is likely that it does not exceed 10%. The filtered cake consisting of 90% calcium sulfite, 5% gypsum and 5% calcium hydroxide is used for land-filling.

State of development A commercial plant to treat 12,000scfm gas from an oil-fired furnace for rock wool production was completed in 1972 and has been in operation since. SO_2 concentration in the gas is reduced from 750 to 25ppm by the scrubbing.

Economics The plant cost $231,000. Estimated costs of larger plants are listed below.

Capacity (scfm)	29,400	58,800	118,000
Investment cost ($)	438,000	711,000	1,156,000

The operation cost assuming that the gas contains 1,500ppm SO_2 and that 95% of the SO_2 is removed is shown below.

	Requirement per ton of oil	Unit cost	Cost $/ton of oil
Sodium hydroxide	13.4 lb	0.032 $/lb	0.428
Milk of lime (carbide sludge)	134 lb	0.0043 $/lb	0.580
Water	0.6t	0.032/ton	0.019
Electric power	66kWh	0.097 $/kWh	0.643
Total			1.67

Advantages High SO_2 removal. No wastewater. No scaling.

Disadvantage Accumulation of sodium sulfate in the liquor necessitates the circulation of the liquor in a large amount.

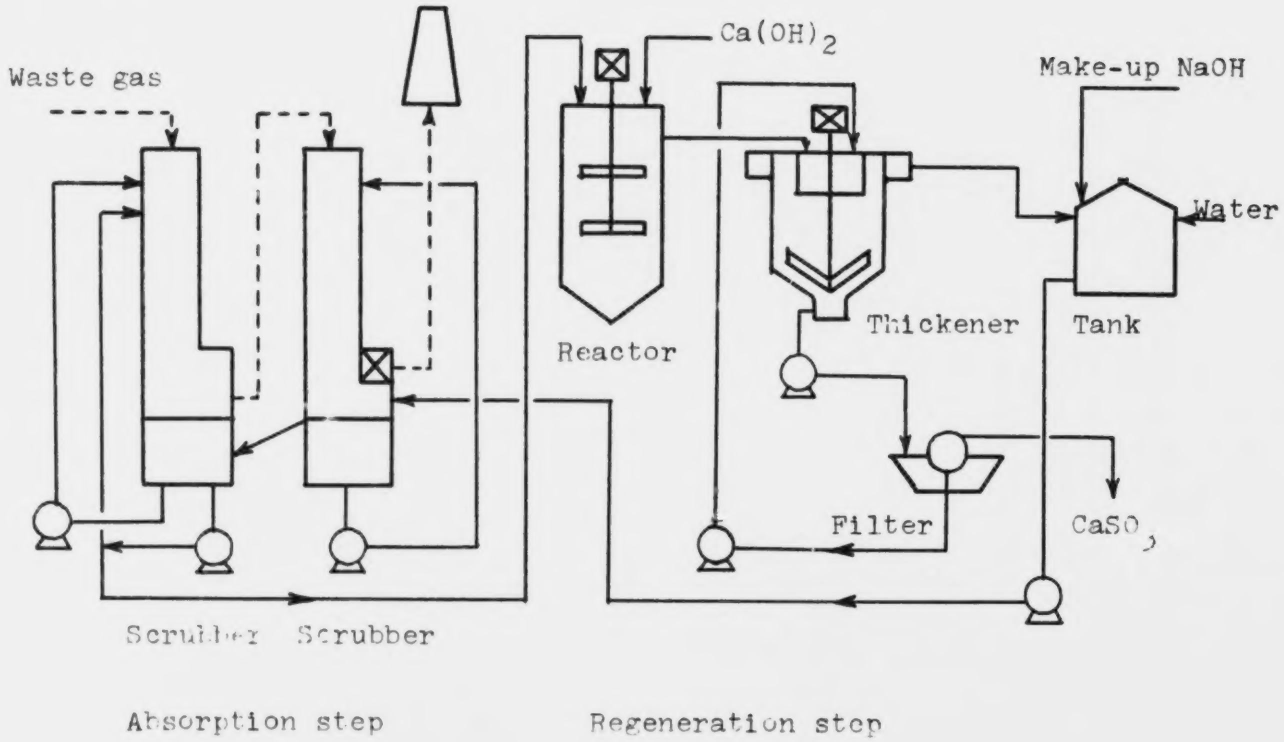

Waste gas
Ca(OH)₂
Make-up NaOH
Water
Reactor
Thickener
Tank
Filter
CaSO₃
Scrubber
Scrubber
Absorption step
Regeneration step

Figure 5.4 Flow sheet of Nippon Steel Chemical sodium-lime process

5.5 NKK ammonia process and ammonia-lime process[7, 8, 9)

Developer Nippon Kokan Kabushiki Kaisha
1-1-3, Otemachi, Chiyodaku, Tokyo

Process description Waste gas at 250°F from an iron ore sintering plant, containing 400 to 1,000ppm SO_2 is first led into an electrostatic precipitator and then cooled to 140°F in a cooler with water spray (Figure 5.5.1). The gas is then led into a screen type scrubber (Jinkoshi type, Figure 5.5.2) for the absorption of SO_2 by a liquor containing ammonium sulfite. In the scrubber 16 mesh screens of stainless steel are placed with some inclination in five stages. On three of the screens placed at the middle of the scrubber, the ammonium sulfite solution flows slowly forming a liquor film which readily absorbs SO_2. On the other two screens placed at the upper part of the scrubber, water flows slowly forming a water film to decrease plume formed by the reaction of SO_2 and ammonia. About 95% of SO_2 is removed when the pH of the circulating liquor is about 6. Virtually no ammonia is lost when the pH of the liquor is 6 or below.

The outlet liquor containing ammonium bisulfite is sent to an ammonia absorber. Coke oven gas containing a small amount of ammonia is introduced into the absorber. The liquor is sprayed to absorb ammonia and to form an ammonium sulfite solution. A large portion of the solution is returned to the scrubber to absorb SO_2. The rest of the solution is sent to an oxidizer where the sulfite is oxidized into sulfate by air bubbles produced by rotary atomizers. The ammonium sulfate solution is evaporated to produce crystal ammonium sulfate.

Nippon Kokan has recently developed an ammonia-lime double alkali process (Figure 5.5.3). The SO_2 absorbing part is the same as in the ammonia process except that no coke oven gas is used. The liquor from the scrubber contains about $(NH_4)_2SO_3$ 7.5%, NH_4HSO_3 7.5% and $(NH_4)_2SO_4$ 15%. A portion of the liquor is sent to a reactor and is reacted with milk of lime (10% concentration) under normal pressure at 210°F. The ammonia released here is sent to the ammonia absorber to be absorbed by the liquor from the scrubber. Calcium sulfate and sulfite are precipitated in the reactor. The slurry from the reactor is acidified with sulfuric acid to adjust the pH to 4 to promote oxidation. The slurry is then led into an oxidizer equipped with rotary atomizers to convert calcium sulfite to gypsum, which is then centrifuged. Salable gypsum with a good quality is obtained. The gas from the oxidizer contains SO_2 and is sent to the scrubber.

State of development After tests with a pilot plant to treat 17,000scfm of waste gas from the iron ore sintering plant, a prototype plant to treat 88,000scfm gas to produce ammonium sulfate by reaction with coke oven gas was completed in early 1972 at the Keihin works of Nippon Kokan.

Additional units for the ammonia-lime double alkali process were completed in November 1972. The construction and the operation of the plants have been carried out as a research project by Japan Iron & Steel Federation.

Status of technology The Jinkoshi type scrubber capable of treating 88,000scfm gas is 56 feet high with a cross section of 14 feet x 23 feet. The following conditions are used for SO_2 absorption:

L/G 12gal/1,000scf Gas velocity 7 to 13ft/sec.

Pressure drop 10 to 12 inches H_2O

Inlet SO_2 400 to 1,000ppm Outlet SO_2 15 to 50ppm

The outlet gas is at 140°F and is not preheated; heavy plume is observed from the stack. Tests have indicated that the plume becomes slight when the gas is reheated to 180°F and nearly invisible at 240°F.

When coke oven gas is used as the source of ammonia, H_2S in the gas is absorbed to form thiosulfate.

$$2H_2S + 2SO_3^{-} + 2HSO_3^{-} \longrightarrow 3S_2O_3^{--} + 3H_2O$$

The thiosulfate is not oxidized into sulfate in the oxidizer. It is decomposed by addition of sulfuric acid to the liquor discharged from the oxidizer.

$$(NH_4)_2S_2O_3 + H_2SO_4 = (NH_4)_2SO_4 + S + SO_2 + H_2O$$

By the decomposition SO_2 is released which is sent to the scrubber. Elemental sulfur formed by the reaction is removed by filtration.

In the ammonia-lime process, the oxidation of calcium sulfite into sulfate is hindered under the presence of thiosulfate. Therefore, it is better not to use coke oven gas in this case. To make up a small amount of ammonia (about 5%) lost from the system, ammonium sulfate is added to the reactor to react with lime and to generate ammonia. The pH in the reactor is maintained at about 11 to ensure gypsum crystal growth in the reactor. To promote the oxidation of calcium sulfite present in the slurry from the reactor, the slurry is acidified to pH 4 by addition of sulfuric acid and then led into the oxidizer. Gypsum grows into big crystals (100 to 300 microns) and can easily be centrifuged to a low moisture content (about 10%). The liquor from the centrifuge which is acidic is neutralized, clarified and returned to the system. No wastewater is emitted.

Advantages The screen type scrubber is effective for SO_2 removal with a relatively low pressure drop. A large amount of gas, up to about 300,000scfm can be treated in one scrubber. By the ammonia process, both SO_2 in waste gas and ammonia in coke oven gas are utilized to produce salable ammonium sulfate. By the ammonia-lime process, salable gypsum of good quality is obtained with no scaling problem. No wastewater is emitted.

Disadvantages When coke oven gas is used, hydrogen sulfide in the gas necessitates additional facilities. The screen in the scrubber is subject to corrosion under inadequate operating condition.

Cost estimation A cost estimation for the ammonia-lime process to treat flue gas from an oil-fired boiler is shown in the following table in comparison with that for the lime-gypsum process developed by Nippon Kokan which is similar to the Mitsubishi-JECCO lime gypsum process (6.1).

Table 5.5 Cost estimation ($1 = ¥308)
(SO_2 in inlet gas 1,400ppm, in outlet gas 70ppm)

	Ammonia-lime process		Lime-gypsum process	
Amount of gas treated (scfm)	235,000	882,000	235,000	882,000
Investment cost ($1,000)	2,110	4,545	2,273	5,844
Fixed cost ($1,000/year)				
Depreciation	382	822	409	1,055
Labor (7 persons)	45	45	45	45
Repair	63	136	68	175
Insurance	2	5	3	7
Management	95	353	84	295
Variable cost ($1,000/year)				
Electric power (@11 mil/kWh)	168	634	191	822
Steam (@$1.5/ton)	96	383		
Industrial water (@15 mil/ton)	4	14	3	11
Seawater (@3 mil/ton)			1	2
Quick lime (@$13.1/ton)	168	688		
Slaked lime (@$15.1/ton)			276	951
Sulfuric acid (@$28.3/ton)	45	180		
Ammonia (@$87.6/ton)	37	148		
Fuel (@$35.1/ton)	326	1,295	262	1,006
Product gypsum (@$5.8/ton)	-226	-899	-220	-883
Desulfurization cost ($/bl)				
With revenue from gypsum	0.69	0.58	0.64	0.52
Without revenue from gypsum	0.82	0.72	0.77	0.66

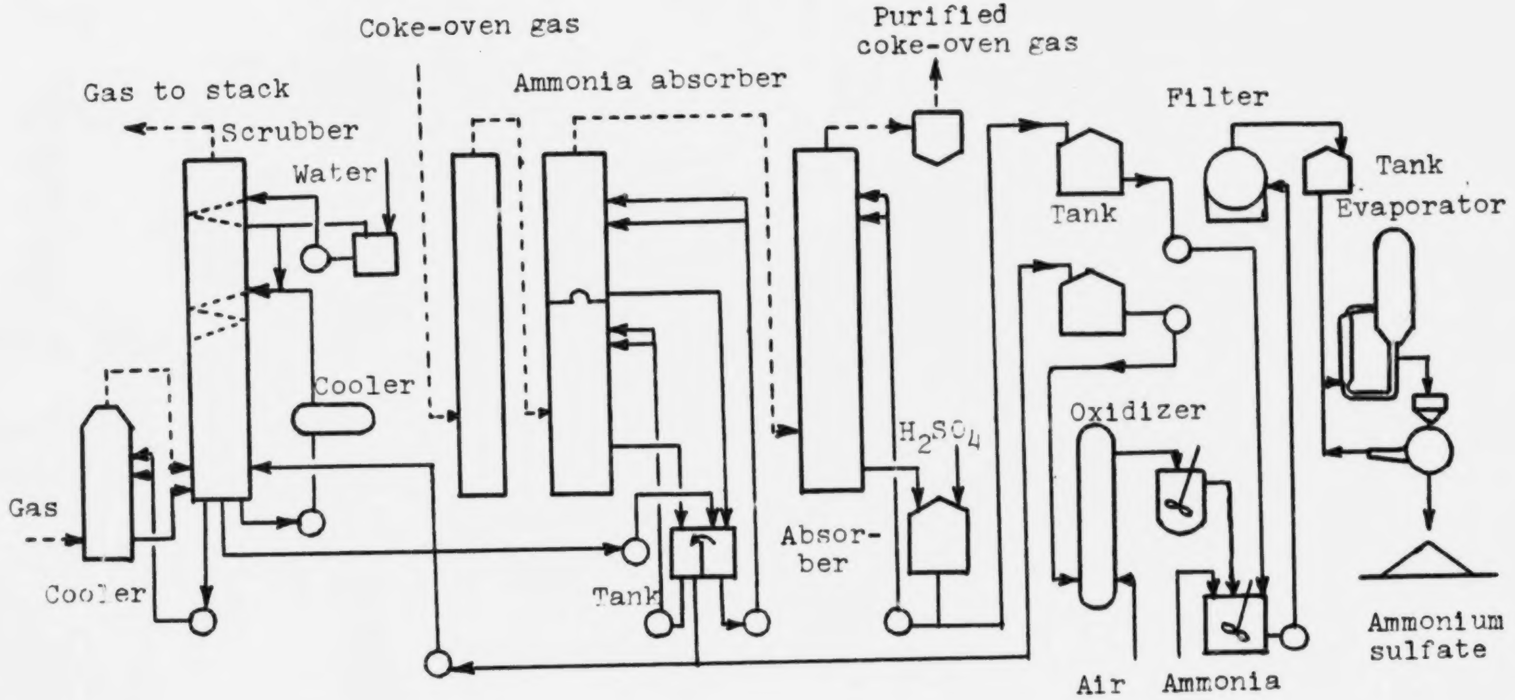

Coke-oven gas
Purified coke-oven gas
Gas to stack
Scrubber
Water
Ammonia absorber
Filter
Tank
Evaporator
Tank
Cooler
Oxidizer
H_2SO_4
Gas
Absor-ber
Tank
Cooler
Ammonium sulfate
Air
Ammonia

Figure 5.5.1 Nippn Kokan ammonium sulfate process

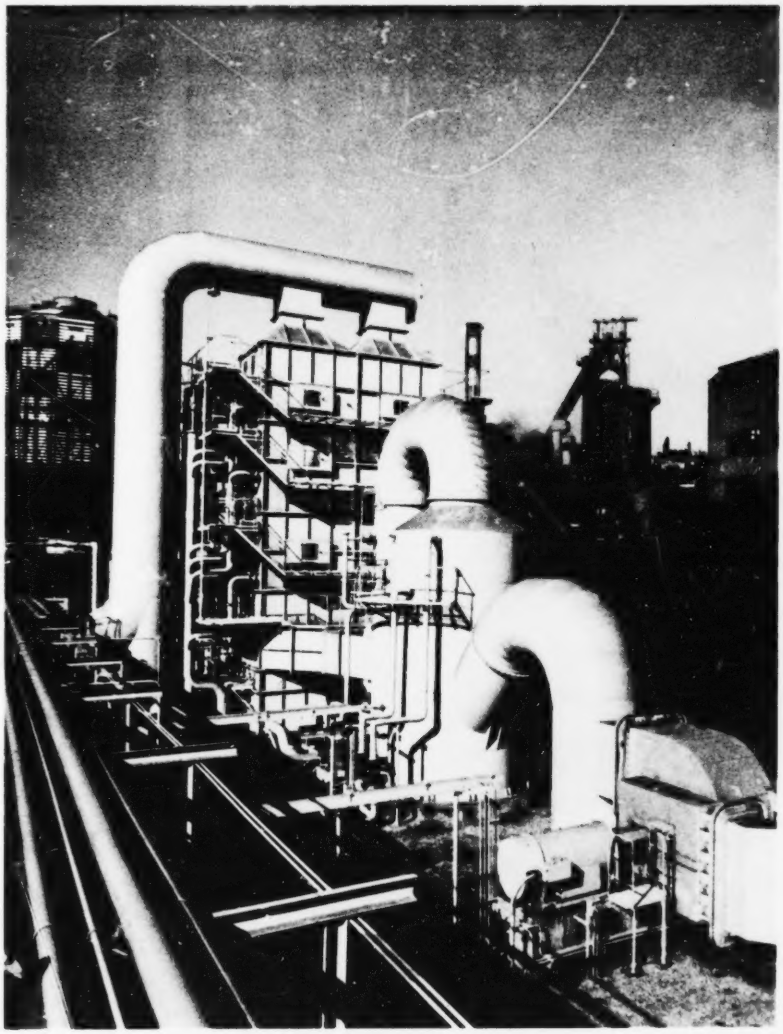


Figure 5.5.2 Keihin plant, Nippon Kokan

(Ammonia scrubbing, 88,000scfm)

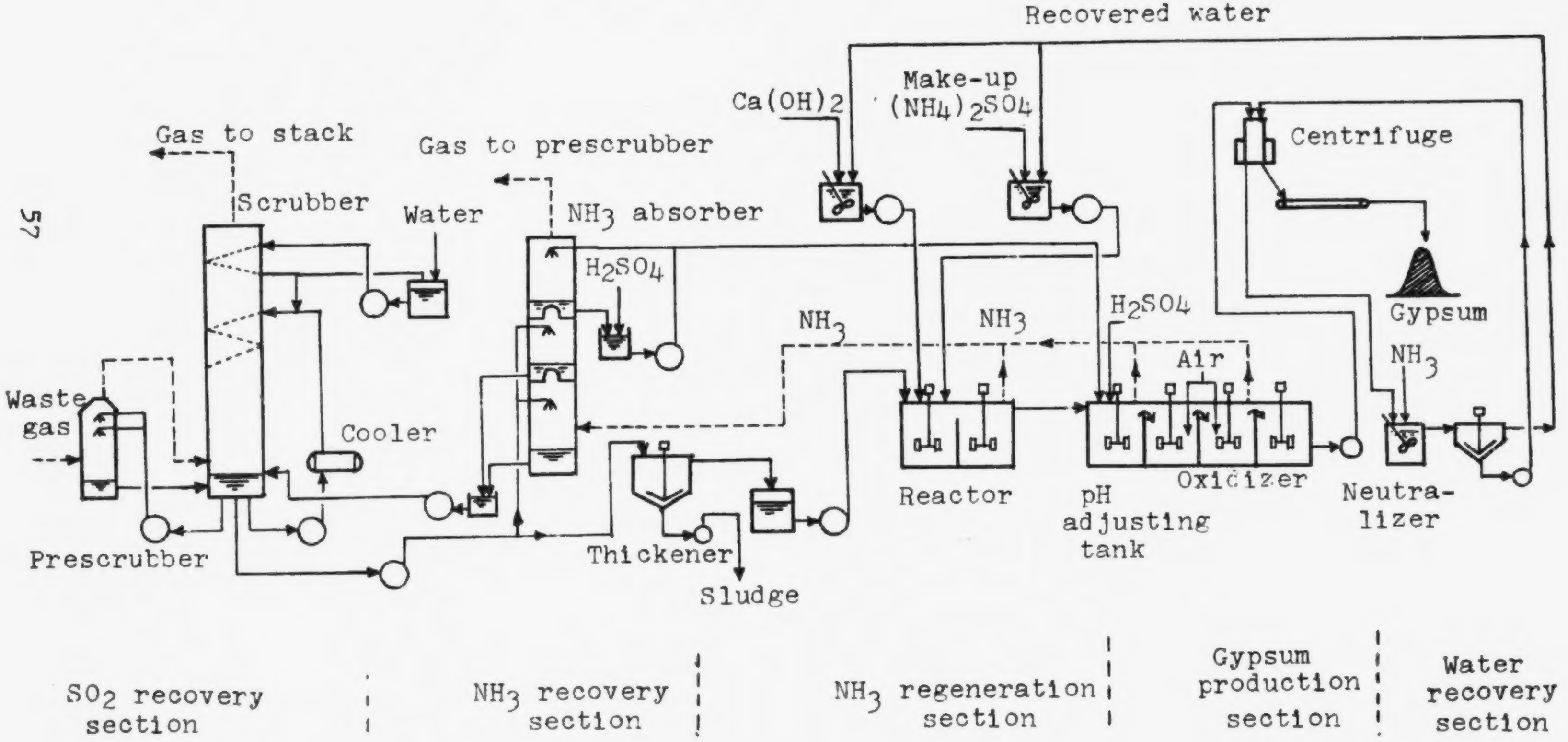

Recovered water
Make-up
$(NH_4)_2SO_4$
$Ca(OH)_2$
Gas to stack
Gas to prescrubber
Scrubber
Water
NH_3 absorber
H_2SO_4
Centrifuge
Gypsum
NH_3
NH_3
H_2SO_4
Air
NH_3
Waste gas
Cooler
Reactor
pH adjusting tank
Oxidizer
Neutralizer
Prescrubber
Thickener
Sludge
SO_2 recovery section
NH_3 recovery section
NH_3 regeneration section
Gypsum production section
Water recovery section

Figure 5.5.3 Nippon Kokan ammonia-lime process

5.6 Wellman-MKK sodium process[7, 8)

Developer Wellman-Lord, U.S.A.

Mitsubishi Chemical Machinery (MKK)
6-2, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Process description Flue gas is first washed by a prescrubber installed in the lower part of the sieve tray absorbtion tower (Figure 5.6.1). The partially cleaned gas rises in the tower while contacting a countercurrent flow of a concentrated sodium sulfite solution which eliminates more than 90% of the inlet SO_2 to form sodium bisulfite. Mist droplets are removed by the eliminator and demister combination in the upper part of the tower and the gas is discharged at about 265°F after reheating in the oil-fired after-burner. A sodium bisulfite solution is discharged from the absorption tower and is stored in a surge tank before it is sumped to an evaporator. In the evaporator the sodium sulfite solution is heated with steam and decomposed into SO_2 gas and sodium sulfite.

$$Na_2SO_3 + SO_2 + H_2O \rightleftarrows 2NaHSO_3$$

The SO_2 concentration in the gas leaving the evaporator is 90% after the water vapor is condensed in a cooler. In this evaporator, sodium sulfite is gradually concentrated and crystallized. The crystalline sodium sulfite is centrifugally separated from the mother liquor, dissolved in a condensate from the cooler, and the solution is recycled to be used as absorbent. The recovered SO_2 is used for sulfuric acid production. Tail gas from the acid plant is led into the absorption tower.

Sodium sulfite is gradually oxidized into sulfate by the oxygen in the flue gas. To keep Na_2SO_4 concentration to a minimum and optimum figure, a small portion of the mother liquor is purged; this purge liquor is used for gas cleaning in the prescrubber. The bleed is taken off this prescrubber circuit for the purpose of removing contaminants, which otherwise would build up in the system. The major contaminants are sodium sulfate and sodium polythionate. The purge stream is subjected to wastewater treatment that involves the following: (1) addition of H_2SO_4 to convert $NaSO_3$ and $NaHSO_3$ to Na_2SO_4; SO_2 evolved is sent to the sulfuric acid plant; (2) alkali is added to form the hydroxide of soluble metal ions (vanadium, nickel, iron); this precipitates them as hydroxides; (3) removal of solids by filtering; (4) neutralization by adding H_2SO_4. The final wastewater is a largely clear concentrated solution of sodium sulfate. This effluent eventually is sent to the bay.

State of development A commercial plant designed to treat 118,000scfm of flue gas from oil-fired boilers has been in operation since June 1971 at Chiba plant, Japan Synthetic Rubber Co. A larger plant with a capacity of treating 365,000scfm of flue gas from oil-fired boilers is under construction at Nishinagoya Station, Chubu Electric Power Co. to start operation in July 1973. It has been recently decided to build a 237,000scfm plant (flue gas from oil-fired boiler) for Japan Synthetic Rubber Co. at Yokkaichi.

Status of technology In Chiba plant, Japan Synthetic Rubber, flue gas from two oil-fired boilers (130 tons/hr each) is treated by two 16-ft square sieve tray absorption towers at a rate of 90,000scfm per absorber. A photograph of the plant is shown in Figure 5.6.2. The plant came on-stream in June 1971 and has been operated for more than 8,000 hours in a year. Figure 5.6.3 shows operation performance of the unit from start-up until March 1972. The SO_2 concentration in inlet gas normally ranges from 1,000 to 2,000ppm and that in outlet gas from 100 to 200ppm.

The major problem associated with the process is the necessity to bleed a waste stream from the absorber liquor circuit to avoid build-up of contaminants, primarily sodium sulfate. The following tabulation summarizes the present composition of absorber and waste streams:

	Absorber feed	Absorber out	Wastewater to treatment	Wastewater after treatment
Na_2SO_3	16-19% by wt	2-4%	0	0
$Na_2S_2O_5$[a]	0	14-17%	4-6%	0
Na_2SO_4	5-7%	5-7%	3-6%	7-16%
Suspended solids	-	-	1-2% (10,000-20,000ppm)	2-10ppm
pH	-	-	5-5.5	7±0.1
COD	-	-	20,000ppm	200ppm
Flow rate	-	-	-	1-1.5 tons/hr

[a] $Na_2S_2O_5 + H_2O \longrightarrow 2NaHSO_3$.

Clear sodium sulfate solution is emitted from Chiba plant. In new plants to be built in future, the sodium sulfate solution will be evaporated to produce solid sodium sulfate as a by-product or treated with lime to precipitate gypsum and to recover a sodium hydroxide solution, thus eliminating the wastewater.

Economics The investment cost of the Chiba plant was $2,600,000 including the cost for sulfuric acid plant. The plant consumes approximately 755,000bbl/year of fuel and produces 13,200 tons/year of sulfuric acid. The requirements of the desulfurization plant are shown below.

Make-up caustic soda	3-4 lb/bl oil for 86-93% recovery of SO_2
After-burner fuel	10.5 lb/bl oil to heat to 266°F
Steam	175 lb/bl oil
Cooling water	6.5 tons/bl oil

The investment cost for Nishinagoya plant, Chubu Electric (365,000scfm) is $5,200,000 including the sulfuric acid plant with a capacity of 90 tons/day.

Advantages Stable reliable operation. High recovery of SO_2. The sulfuric-acid plant is much smaller than usual because the concentrated SO_2 recovered is used.

Disadvantage The treatment of sodium sulfate formed by the oxidation is not simple.

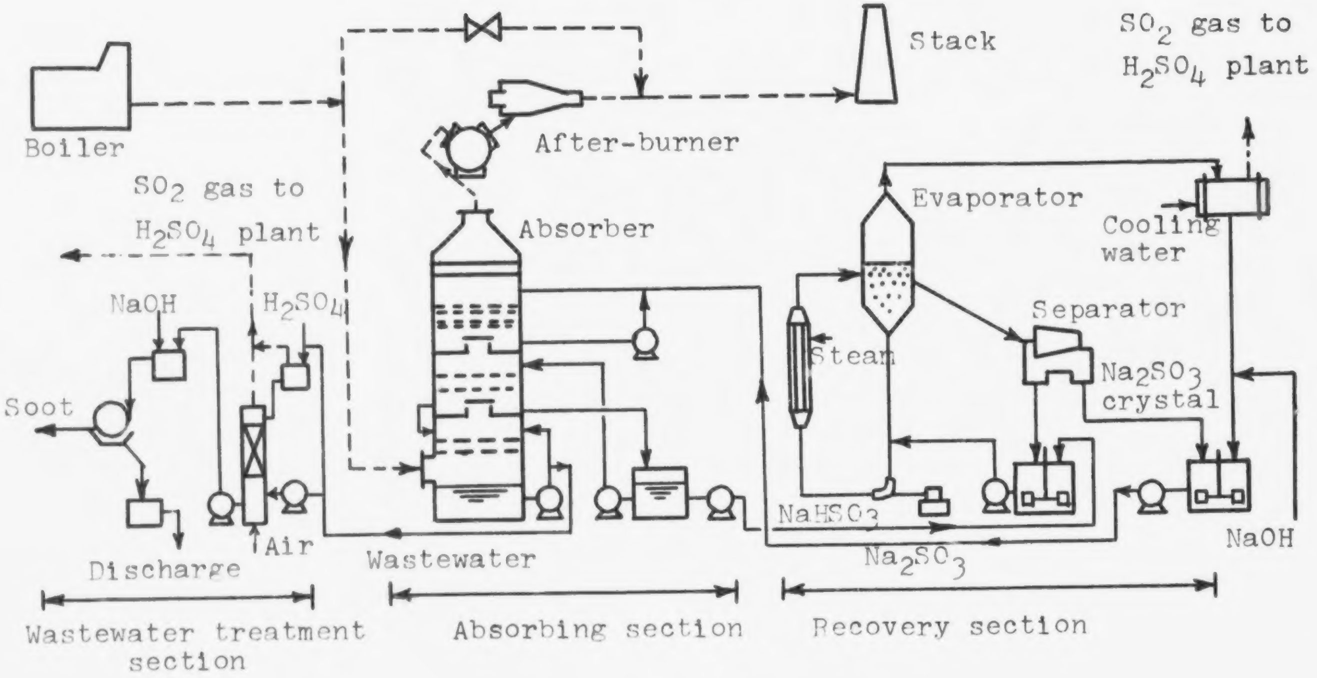

Boiler
SO$_2$ gas to H$_2$SO$_4$ plant
After-burner
Stack
SO$_2$ gas to H$_2$SO$_4$ plant
Evaporator
Absorber
Cooling water
NaOH
H$_2$SO$_4$
Separator
Steam
Na$_2$SO$_3$ crystal
Soot
Air
Discharge
Wastewater
NaHSO$_3$
Na$_2$SO$_3$
NaOH
Wastewater treatment section
Absorbing section
Recovery section

Figure 5.6.1 Wellman-MKK process

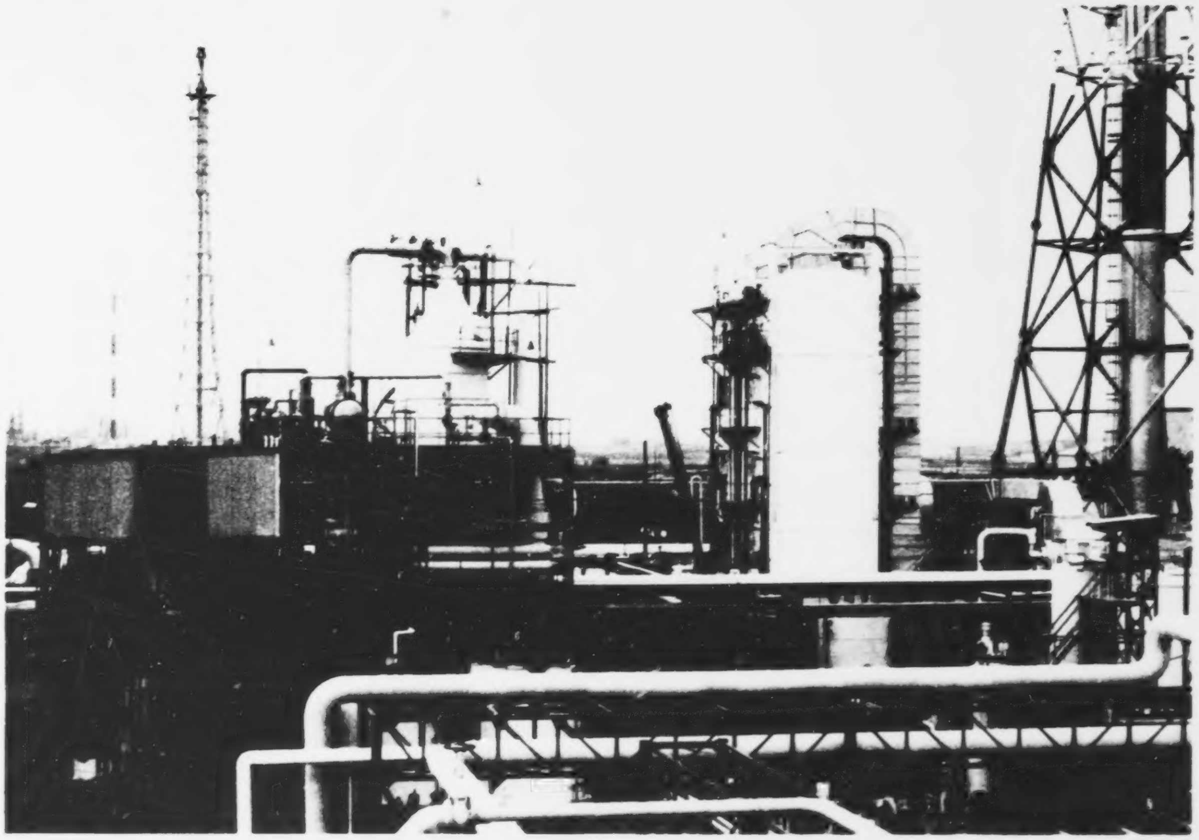


Figure 5.6.2 Chiba plant, Japan Synthetic Rubber
(Wellman-MKK process)

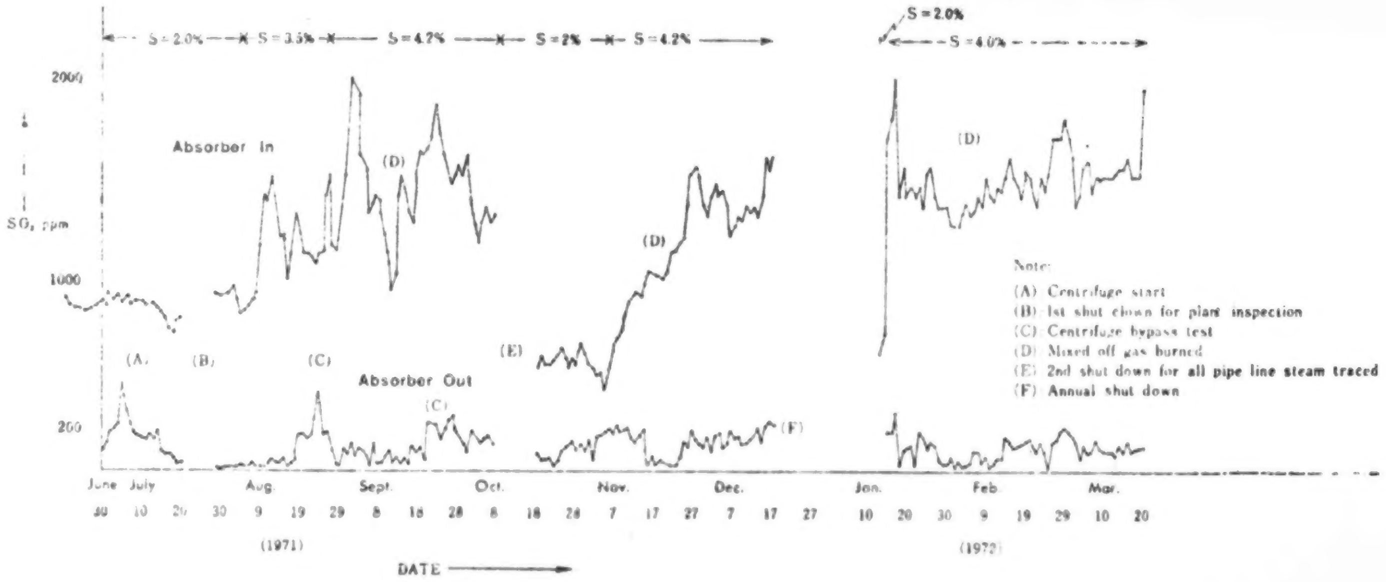


Figure 5.6.3 Actual operation results of Wellman-MKK plant at Japan Synthetic Rubber's Chiba factory

5.7 Wellman-SCEC sodium process

Developer Wellman-Lord, U.S.A.

Sumitomo Chemical Engineering Co. (SCEC)
33-5, 3-chome, Hongo, Bunkyo-ku, Tokyo

Process description Tail gas from a Claus furnace, 38,800scfm at 930°F, containing about 7,000ppm SO_2 is cooled to 660°F in a waste-heat boiler, to 210°F in a cooling tower with water spray, and then to 160°F in a heat exchanger. This cooling method was used because gas containing much SO_2 at 210-660°F is quite corrosive. The cooled gas is introduced into an absorber with a three-stage sieve tray to which a sodium sulfite solution at pH 6.2 to 6.4 is charged. About 93% of SO_2 is recovered in the absorber.

Sodium bisulfite solution at pH 5.7 to 6.0 is discharged from the absorber, led to an evaporating crystallizer, and heated to 210°F to separate a gas (50% SO_2 and 50% water vapor) and crystalline sodium sulfite from the solution. The gas is cooled in a condenser to remove water. The product gas, which contains more than 99% SO_2, is sent to a Claus furnace. The solid sodium sulfite is dissolved in water from the condenser and returned to the abosrber. The remaining solution is recycled to the crystallizer. A portion of the solution is taken out of the system to remove impurities and the sodium sulfate formed by oxidation.

An oxidation inhibitor developed by Sumitomo Chemical Co. has been used in the process. Without the inhibitor 3 to 5% of total sodium compounds in the plant is converted to sulfate in a day. By the use of the inhibitor, oxidation is reduced to about 40% resulting in a substantial decrease in the consumption of sodium hydroxide. The use of the inhibitor has been licensed by Sumitomo Chemical Co. to Wellman-Lord recently.

State of development A commercial plant designed to treat 38,800scfm of tail gas from a Claus furnace has been in operation since July 1971 at Negishi Refinery, Toa Nenryo to return the recovered SO_2 to the Claus furnace. Another plant with a capacity of treating 212,000scfm of flue gas from an oil-fired boiler is under construction at Chiba plant, Sumitomo Chiba Chemical; the recovered SO_2 will be used for sulfuric acid production.

Advantages Stable operation and high recovery of SO_2. Formation of sodium sulfate is substantially reduced by the use of the oxidation inhibitor.

Disadvantage Treatment of sodium sulfate is not simple even though the amount of the sulfate is reduced by the use of the inhibitor. Cooling of the high-temperature gas containing much SO_2 is not simple because of its corrosiveness.

Economics The total investment cost for the 38,800-scfm plant was \$1.94 million. In addition, \$0.64 million was required for the cooling system for the tail gas including a waste-heat boiler, cooling tower, and heat exchanger.

It is estimated by Sumitomo Chemical Engineering that when this type of desulfurization plant is used for a 250MW oil-fired power plant to treat 441,000scfm of flue gas, the cost to remove 90% of SO_2 would be about \$0.78/bl of oil. Reheating of the waste gas by an after-burner would require \$0.1 - 0.15 more.

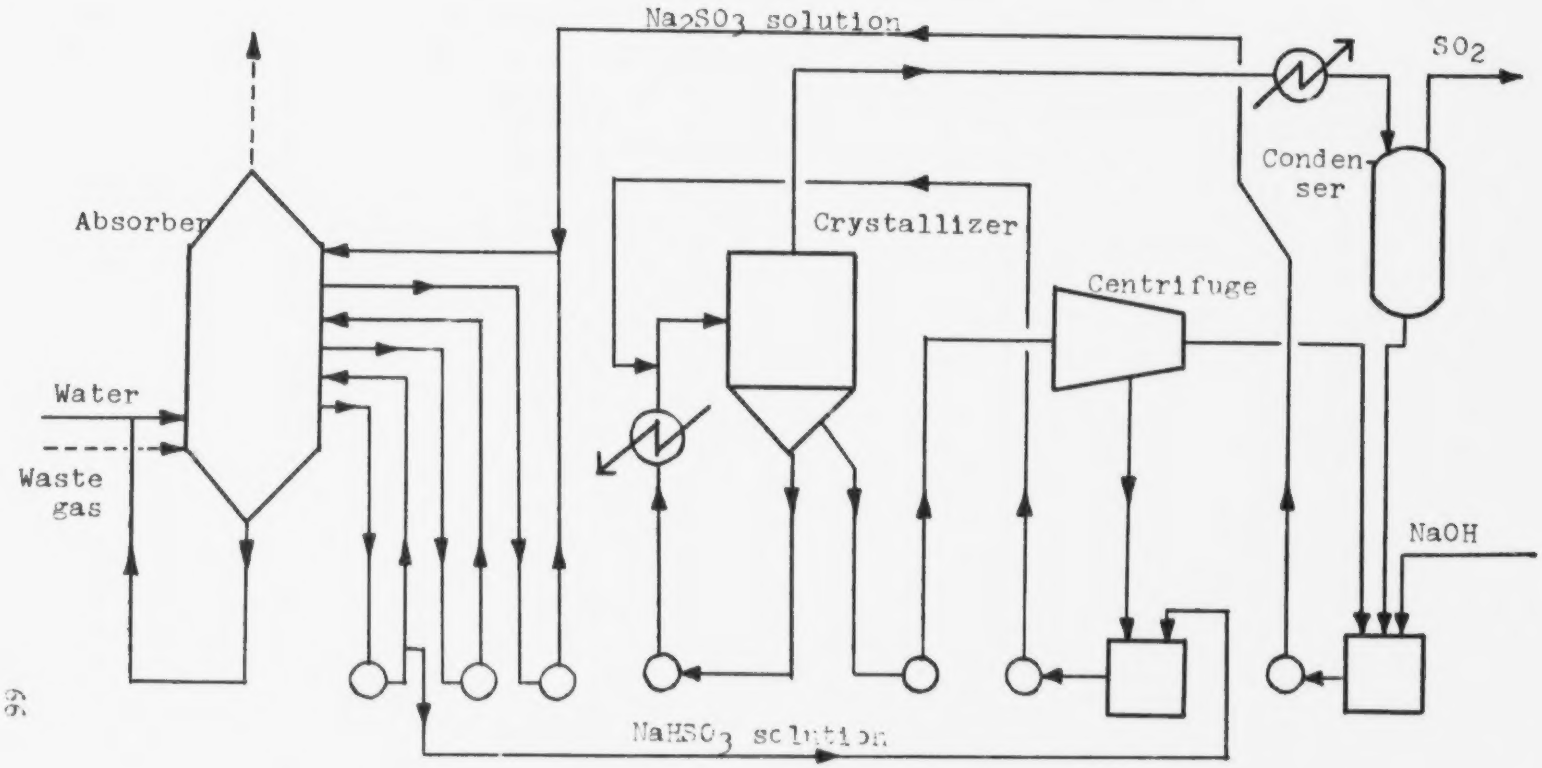

Na$_2$SO$_3$ solution
SO$_2$
Conden-
ser
Absorber
Crystallizer
Centrifuge
Water
Waste
gas
NaOH
NaHSO$_3$ solution

Figure 5.7 Flow sheet of Wellman-SCEC process

5.8 Oji sodium process[7)]

Developer Oji Paper Co.
4-7-5, Ginza, Chuo-ku, Tokyo

Process description Oji has constructed many sodium scrubbing plants to produce sodium sulfite for paper mills by using OK scrubbers developed by Oji and also Jinkoshi scrubbers developed by Kanagawa PIL. The OK scrubber is of the spray type and has been used mainly for the treatment of waste gas from kraft recovery boilers. Up to about 150,000scfm gas can be treated by the scrubber to remove 95% SO_2 and 70 to 90% of dust from the recovery boiler gas with a pressure drop of 2 to 2.5 in. H_2O. The Jinkoshi scrubber is of the screen type and has been used for flue gas from oil-fired boilers.

The OK scrubber was described in the 1972 report by the present author. A flow sheet of a prototype plant (265,000scfm) with Jinkoshi scrubbers is shown in Figure 5.6. The gas is first treated by a prescrubber in which screens (about 10 mesh, made of stainless steel SAS 33) are placed nearly vertically. The screens are set in frames about 3.3 feet wide and 7 to 10 feet long. Water flows slowly on the screens forming films. Dust is removed and the gas is moistened by the water films. The gas is then led into a scrubber where screens are placed with inclination. The scrubber is 12 feet wide, 14 feet deep and 36 feet high. A sodium sulfite solution with some sodium hydroxide is fed onto the screen to form films to absorb SO_2 giving a solution of sodium sulfite. Most of the sulfite solution is recycled with addition of sodium hydroxide; a portion of the sulfite solution is bypassed and obtained as a product to be used for paper mills. SO_2 removal was about 80% with three stages of screens and 95% with nine stages when the gas velocity in the scrubber was between 2 and 12 feet/sec; desulfurization was not appreciably affected by the gas velocity within the above range. The pressure drop per stage of screen was 0.5 in. H_2O at a gas velocity of 3 feet/sec and 0.6 in. H_2O at 12 feet/sec.

As the liquor in the prescrubber became acidic and corroded the screens, the prescrubber was eliminated in commercial plants in which the gas is cooled with water sprays and fed to a scrubber. A scrubber to treat 130,000scfm of flue gas is 23 feet wide, 17 feet deep and 36 feet high.

State of development The following plants have been in operation:

Commercial plants by Oji process

Type of scrubber	User	Plant site	Number of scrubbers	Capacity (1,000scfm)	Date of completion
OK	Oji	Kasugai	8	628	1966 to 1969
OK	Tokai		3	204	1970
OK	Oji	Kasugai	1	118*	1970
OK	Chuetsu	Sendai	1	68	1971
OK	Honshu	Kushiro	2	153	1971
OK	Oji	Ebetsu	1	108*	1971
OK	Oji	Mishima	6	470	1972
Jinkoshi	Oji	Tomakomai	2	288*	1971
Jinkoshi	Oji	Tomakomai	2	306*	1972

* For oil-burning boilers. Others are for kraft recovery boilers.

Advantages The OK scrubber is simple and cheap. It features a small pressure drop (1.5 to 2.5 in. H_2O). The Jinkoshi scrubber is quite effective for SO_2 recovery and dust removal with a small power consumption.

Disadvantages Demand for sodium sulfite is limited. The screens of the Jinkoshi scrubber undergo corrosion when the scrubber is not operated properly.

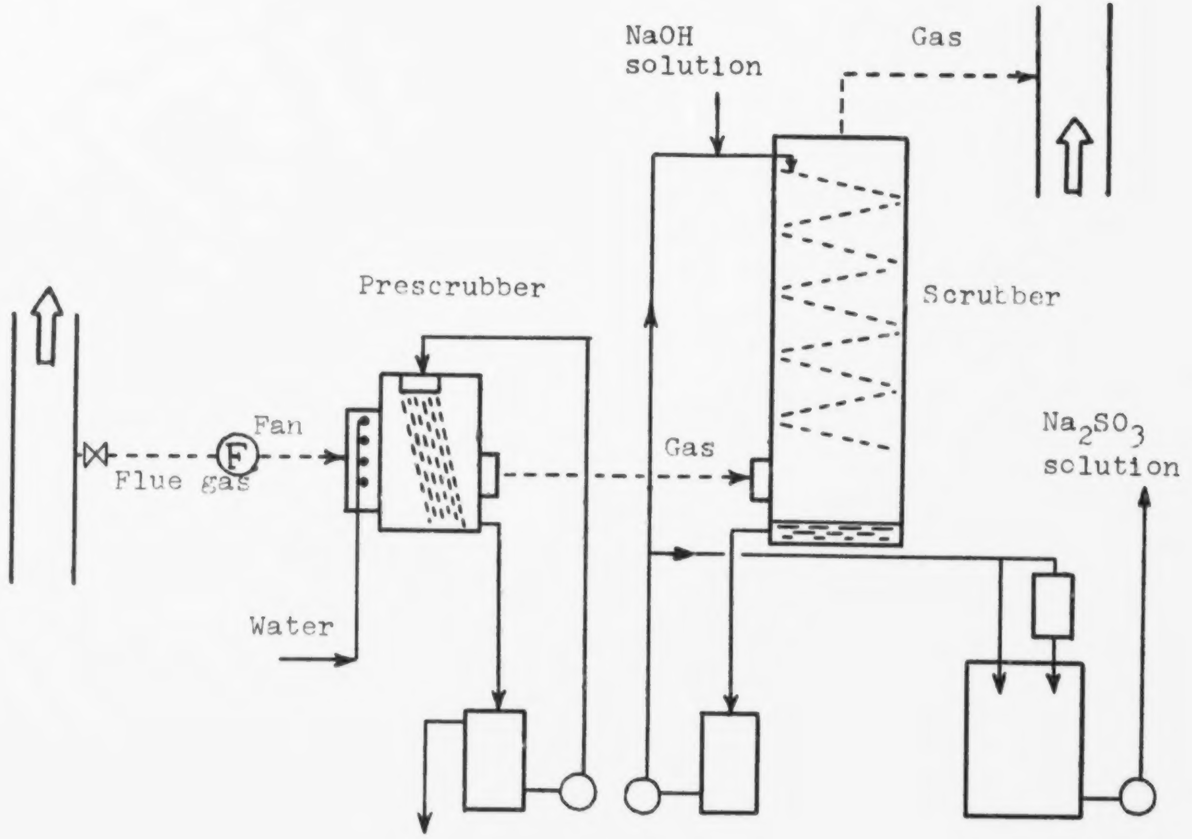

NaOH solution
Gas
Prescrubber
Scrubber
Fan
F
Flue gas
Gas
Na_2SO_3 solution
Water

Figure 5.8 Flow sheet of prototype plant by Jinkoshi-Oji process

5.9 Tsukishima sodium process[7)]

Developer Tsukishima Kikai Co.
17-15, 2-chome, Tsukuda, Chuo-ku, Tokyo

Process description SO_2 in waste gas is absorbed by a sodium sulfite solution to form sodium bisulfite. The bisulfite solution is neutralized with sodium hydroxide to form the sulfite. A portion of the sulfite solution is recycled to the absorption system; the rest if filtered to remove dust and is obtained as by-product sodium sulfite (solution or solid) to be used for paper mills. Otherwise, the sulfite solution is oxidized with air by an oxidizer to produce sodium sulfate which is either discarded in solution form or utilized as solid sodium sulfate. More than 90% of SO_2 is removed.

State of development More than 20 plants are in operation. Some of the larger ones are shown in Table 5.9.

Advantages The process is simple and operation is easy. The Bahco scrubber is effective not only for SO_2 removal but also for elimination of dust.

Disadvantages Demand for sodium sulfite and sulfate is limited. Sodium hydroxide is fairly expensive. Restrictions on sodium sulfate emission might become stringent in future.

Table 5.9 Desulfurization plants by Tsukishima

User	Plant site	Capacity (1,000scfm)	SO_2 (ppm)	Type of absorber	Product	Year of completion
Shimura Kako	Muroran	11.7[a]	18,000	Bubbling	Na_2SO_3(solid)	1970
Sumitomo Mining	Toyo	82.3[b]		TCA	Na_2SO_3(solid)	1970
Sumitomo Mining	Besshi	88.2[a]		Packed tower	Na_2SO_3(solid)	1970
Mitsui Senpoku Oil	Sakai	8.8[c]	4,000	Packed tower	Na_2SO_4(solid)	1971
Daishowa Paper	Yoshinaga	129.4[d]	1,700	Bahco	Na_2SO_3(solution)	1971
Hiroshima City	Hiroshima	10.5[e]	1,000	Bahco	Na_2SO_4(waste)	1971
Osake City	Osaka	10.5[e]	1,000	Bahco	Na_2SO_4(waste)	1971
Yahagi Iron	Nagoya	47.0[f]	4,000	Bahco	Gypsum	1971
Daio Paper	Iyomishima	70.6[d]	1,700	Bahco	Na_2SO_3(solution)	1972
Daio Paper	Iyomishima	88.2[d]	1,700	Bahco	Na_2SO_3(solution)	1972
Tokyo Metropolis	Odai	117.6[e]	1,000	Spray tower	Na_2SO_4 (waste)	1972
Daishowa Paper	Yoshinaga	97.1[d]	1,700	Bahco	Na_2SO_3 (solution)	1972

a; Smelting plant b: Sulfuric acid plant c: Claus furnace

d: Oil-fired boiler e: City-mud burning f: Iron-ore pelletizing plant

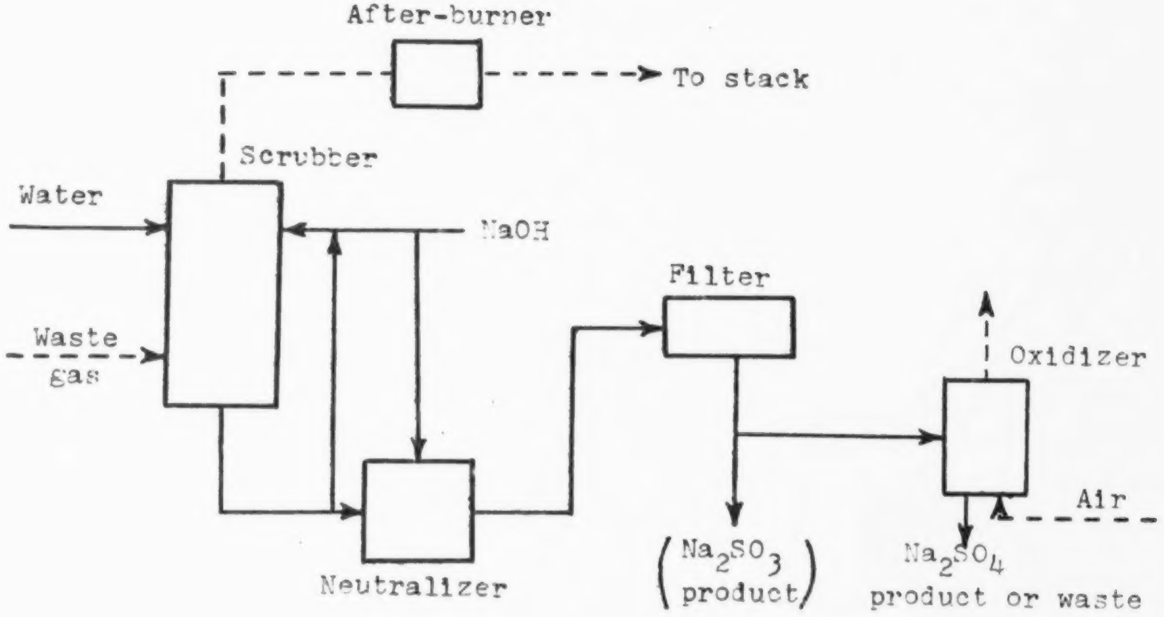

After-burner
To stack
Scrubber
Water
NaOH
Waste gas
Filter
Oxidizer
Air
Neutralizer
$\left(\begin{array}{c}Na_2SO_3\\ \text{product}\end{array}\right)$
Na_2SO_4 product or waste

Figure 5.9 Simplified flow sheet of Tsukishima process

5.10 IHI-TCA sodium process7)

Developer Ishikawajima-Harima Heavy Industries Ltd.
2-2-1, Otemachi, Chiyoda-ku, Tokyo

Process description Flue gas from a boiler is first cooled in a cooler with water spray and then introduced into a turbulent contact absorber (TCA scrubber, in two stages) with polypropylene balls to absorb SO_2 with a sodium sulfite solution. More than 90% of the SO_2 is removed. The sodium bisulfite solution thus formed is then reacted with sodium hydroxide to produce a sodium sulfite solution, a portion of which is returned to the absorber and the rest is fed to an oxidizer after being filtered to remove dust. The oxidizer is provided with an atomizer invented by IHI and called "Smoke Atomizer." Compressed air at 5 to 6 atmospheric pressure is introduced into the atomizer to give many small bubbles. Sodium sulfite is oxidized into sulfate which is either abandoned with wastewater or recovered to produce salable sulfate. The concentration of the sulfate solution from the oxidizer is about 15% to give the waste product, and higher to give the salable product.

State of development A unit with a capacity of treating 35,000scfm flue gas to recover sodium sulfate was built at Yokohama plant, Tsurumi Soda Co. in 1971. Three units each with a capacity of treating 88,000scfm flue gas to recover sodium sulfate are under construction at Sakai plant of Mitsui Senpoku Oil Co. Several units have been built recently to produce waste sodium sulfate solution, including one in Oppama plant, Nissan Motor Co. with a capacity of treating 67,000scfm flue gas and smaller ones.

Advantages High recovery or removal of SO_2 is achieved. Operation as well as maintenance is easy.

Disadvantages Sodium hydroxide is expensive. Demand for sodium sulfate is limited.

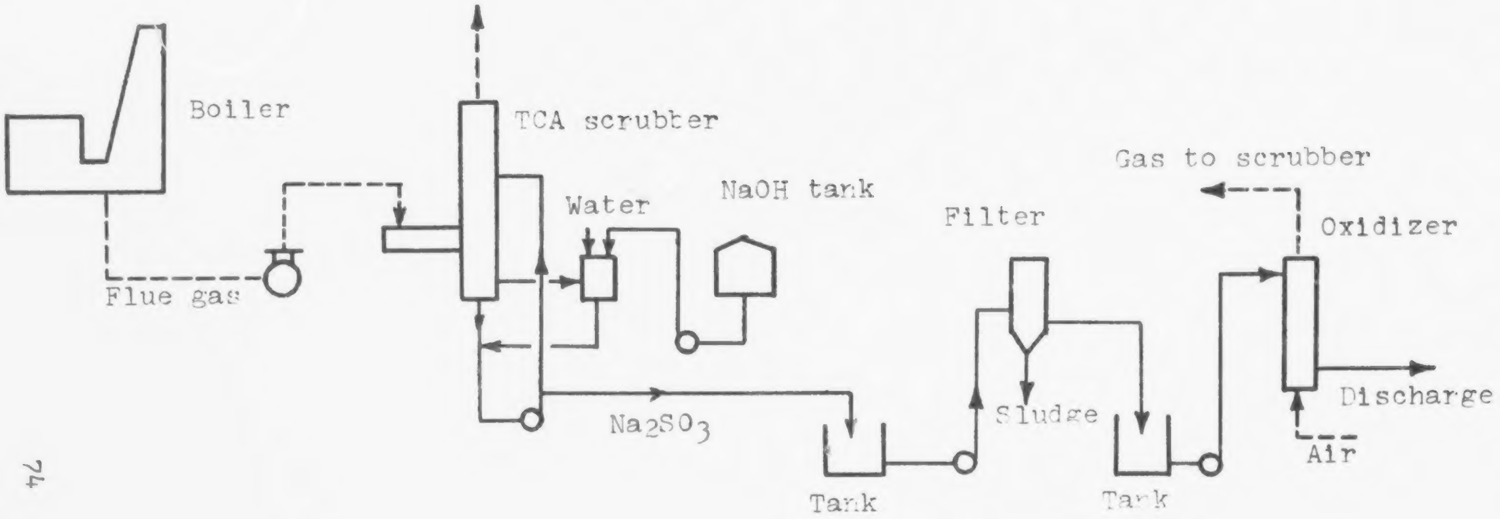

Boiler
Flue gas
TCA scrubber
Water
NaOH tank
Na_2SO_3
Tank
Filter
Sludge
Tank
Gas to scrubber
Oxidizer
Discharge
Air

Figure 5.10 Flow sheet of IHI-TCA sodium process (waste Na_2SO_4)

5.11 MKK sodium process (Evergreen process)

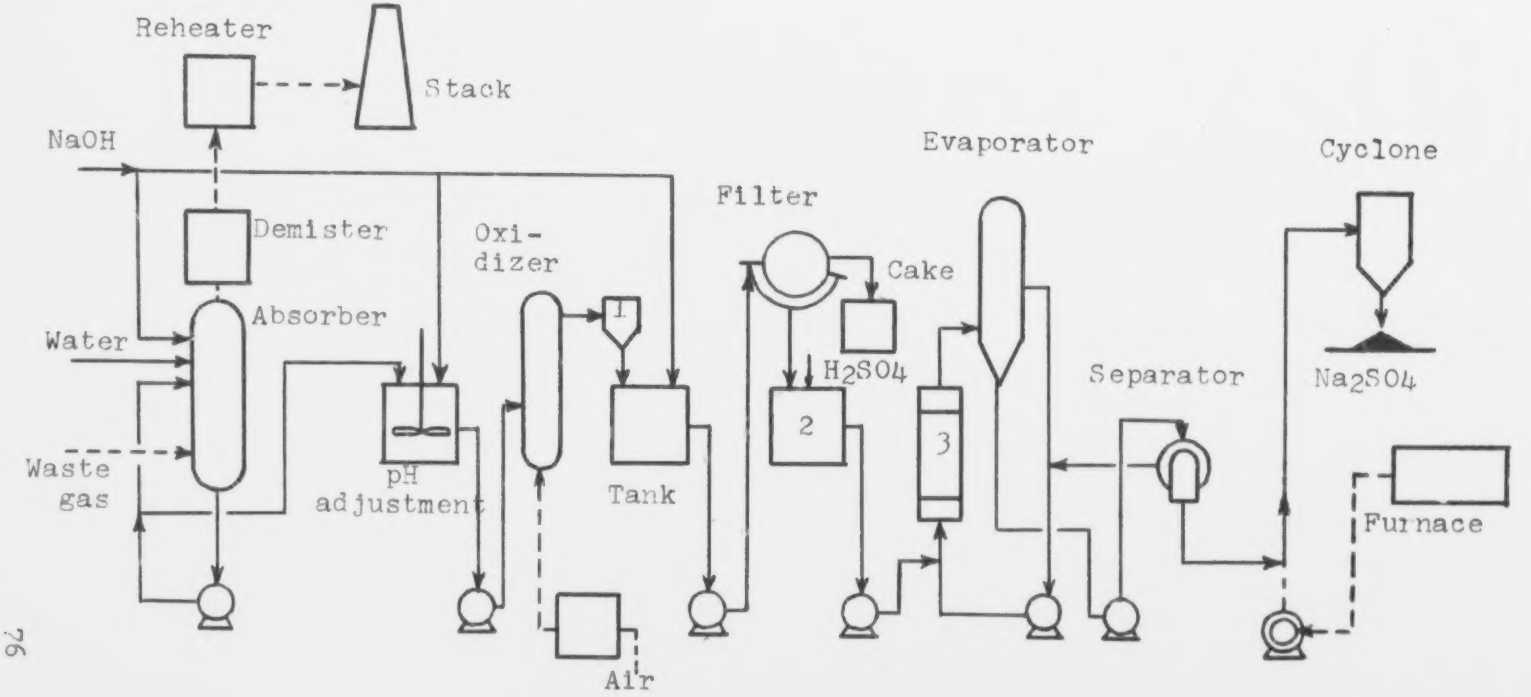
Developer Mitsubishi Chemical Machinery (MKK)
6-2, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Process description Waste gas from glass melting plant is treated in an absorber with a sodium hydroxide solution (Figure 5.9). More than 97% of SO_2 is recovered to form sodium sulfite. Most of the dust in the gas consisting mainly of very small particles of sodium sulfate and also most of the SO_3 mist in the gas are recovered by the solution and by a special mist eliminator placed at the upper part of the absorber. The bisulfite solution is neutralized with sodium hydroxide to regenerate the sodium sulfite solution which is partly returned to the absorber and partly sent to an oxidizer after pH adjustment. In the oxidizer, the sulfite solution is oxidized into sulfate by air. Heavy metals derived from the dust and dissolved in the solution are precipitated by raising pH with sodium hydroxide. The precipitate and the dust are then filtered off. The filtrate is neutralized with sulfuric acid and evaporated. Anhydrous sodium sulfate is crystallized from the solution, centrifuged, dried in a flash dryer, and caught by a cyclone. The product sodium sulfate is of high purity and is used for glass production.

State of development A commercial plant with a capacity of treating 41,000scfm gas from a glass melting furnace at Kansai Factory, Asahi Glass Co. has been in continuous operation since its start in November 1972. Another plant (129,000scfm), under construction at Keihin Factory, Asahi Glass Co., is to come on-stream in June 1973.

Advantages High recovery of SO_2 and dust is attained. The process is simple and operation is easy. No water is wasted.

Disadvantage Demand for sodium sulfate is limited.


Reheater
Stack
NaOH
Demister
Absorber
Water
Waste gas
pH adjustment
Oxi- dizer
1
Air
Tank
Filter
Cake
H_2SO4
2
Evaporator
3
Separator
Cyclone
Na_2SO4
Furnace

1: Mist separator   2: Neutralization tank   3: Heater

Figure 5.11 Flow sheet of Evergreen process (Na_2SO_4 recovery)

5.12 Kurabo sodium process and ammonia-lime process7)

Developer Kurabo Industries
2-41, Kitakyutaromachi, Higashi-ku, Osaka

Process description SO_2 in waste gas is absorbed by sodium sulfite or waste alkaline solution in a special type of scrubber (KCBA scrubber) developed by Kurabo. The reacted solution is neutralized by sodium hydroxide or waste alkali and then oxidized at 50 to 60°C by introducing air under normal pressure using a small amount of catalyst to convert sodium sulfite to sulfate. The sulfate solution is abandoned with other wastewater. Ammonia is also used for SO_2 removal, to produce waste ammonium sulfate solution.

The KCBA scrubber resembles a multijet scrubber (Figure 5.12). The gas to be treated is first mixed with the solution in a scrubber consisting of a diffuser and header, and then led into a solution tank in fine bubbles. The gas is then passed through a demister and reheated to 230°F by an after-burner. For the oxidation, vessels similar to the KCBA scrubber are used. Kurabo has recently been working on a double alkali process using ammonia and lime. An ammonium sulfite solution (5% concentration) is used for the absorption. The ammonium bisulfite solution thus formed is neutralized with ammonia to form ammonium sulfite, which is then oxidized into sulfate. Slaked lime is added to the sulfate solution to precipitate gypsum and to recover ammonia. Salable gypsum of a good quality is obtained. Pressure drop in the scrubber is between 2 and 4 inches H_2O.

State of development More than 30 commercial plants using waste alkali or sodium scrubbing and two commercial plants using ammonia scrubbing are in operation to treat waste gas from chemical plants and small boilers. Many others are under construction. The unit capacity ranges from 3,000 to 35,000scfm. Some of the larger units are listed in Table 4.4. The ammonia scrubbing unit at Amagasaki plant, Mitsubishi Electric Co. features very light plume which is almost invisible. Low concentration and low temperature (40°C) of the solution may help plume abatement. For the ammonia-lime process a pilot plant with a capacity of 2,900scfm is in operation but there is not yet a definite plan to build larger plants.

Size of the KCBA The sizes of KCBA scrubber tanks are shown in Table 5.12.1.

Table 5.12.1 Sizes of KCBA scrubber tanks

	Size in feet		
Capacity(scfm)	Width	Length	Height
3,000	4.7	12.8	8.6
12,000	8.4	12.8	8.6
35,000	22.8	13.8	8.6

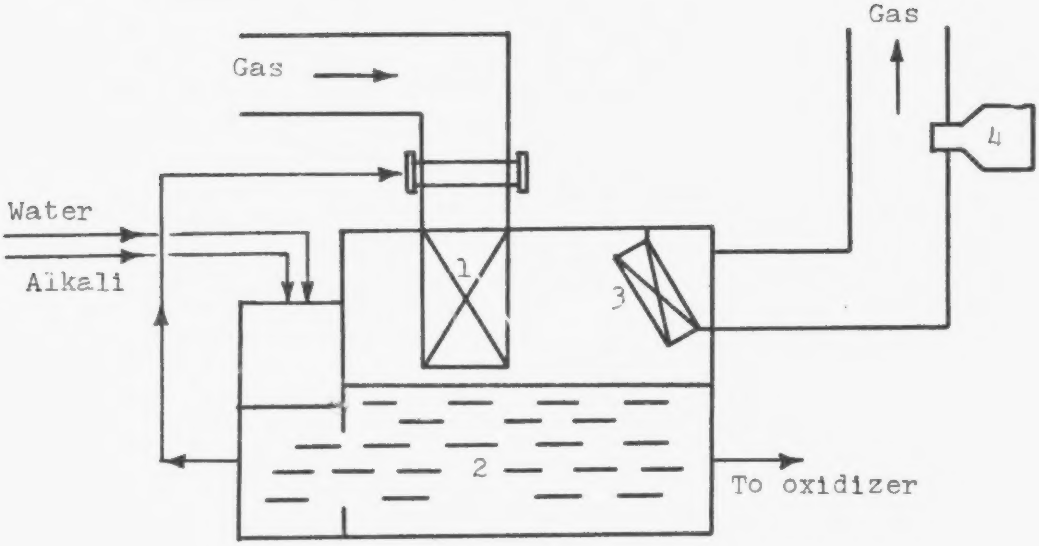
Economics A cost estimation is shown in Table 5.12.2.

Table 5.12.2 Cost estimation for Kurabo Processes
(Sulfur in heavy oil 2.5%; SO_2 removal 90%; Slaked lime $20/t;
By-produced gypsum $6/t)

Capacity (1,000scfm)	35	35	35	59
Absorbent	NaOH	NaOH	NH_3 $Ca(OH)_2$	NH_3 $Ca(OH)_2$
Product	Waste Na_2SO_3	Waste Na_2SO_4	Gypsum	Gypsum
Investment cost ($1,000)	130	195	390	550
Annual cost ($1,000)				
Fixed cost	23	33	68	98
Running cost	140	182	146	218
By-product revenue	0	0	-26	-46
Total	163	215	188	270
Desulfurization cost				
($/MWh)	1.38	1.95	1.58	1.38
($/bl)	0.88	1.25	1.00	0.88

Advantages The KCBA scrubbers are effective in removing SO_2 and also dust. Less plume from ammonia process is another advantage.

Disadvantage The scrubber requires a fairly large floor space and may not suit very large plants.


Gas
Gas
4
Water
Alkali
1
3
2
To oxidizer

1: Diffuser and header 2: Liquor tank

3: Demister 4: After-burner

Figure 5.12 KCBA scrubber

5.13 Other sodium processes

5.13.1 Toyobo process

Toyobo Engineering Co. (2-8, Hamadori, Dojima, Kita-ku, Osaka) has developed a TVR scrubber, which is a combination of a spray tower and a special absorber, and has built two commercial plants recently to remove SO_2 in flue gas from industrial boilers (24,000 and 26,000scfm). Waste alkaline solution is used as the absorbent; waste sodium sulfite solution is produced (Table 4.4).

5.13.2 Kawasaki process

Kawasaki Heavy Industries (16-1, 2-chome, Nakamachidori, Ikeda-ku, Kobe) has recently built three sodium-scrubbing plants, each with a capacity of treating 17,000-34,000scfm gas by Solivore scrubbers (see 7.4). In one of the plants sodium sulfite is recovered; waste solutions of sodium sulfite and sulfate are produced in the other two plants.

5.13.3 Gadelius process

Gadelius Co. Ltd. (4-5, Kojimachi, Chiyoda-ku, Tokyo) has recently built several sodium-scrubbing plants using SF-venturi scrubbers (Table 4.1).

6 Wet-lime (limestone) process

6.1 Mitsubishi-JECCO lime (limestone)-gypsum process[7, 8]

Developer Mitsubishi Heavy Industries
5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Japan Engineering Consulting Co.
1-4, Ogawamachi, Kanda, Chiyoda-ku, Tokyo

Process description Waste gas is first washed with water for dust removal and cooling to about 140°F. As the water becomes acidic and dissolves metallic components of dust, it is neutralized with milk of lime to precipitate metallic ions, which are filtered off together with the dust. The filtrate is used for slaking of lime. The cooled gas is then sent to an absorbing step. At three plants built recently two plastic-grid packed absorbers in series, which are put together in one tower, are used as shown in Figures 6.1.1 and 6.1.2. (For new plants which are being designed a one-absorber system will be used.) Milk of lime is fed to the No. 2 absorber. The gas is introduced into the No. 1 absorber and then into the No. 2 absorber. The slurry discharged from the No. 2 absorber is a mixture of calcium sulfite and unreacted lime with a small amount of gypsum. The slurry is then led to the No. 1 absorber, where the remaining lime is reacted to form calcium sulfite, a portion of the sulfite is converted to bisulfite. The pH of the slurry discharged from the No. 1 absorber is 4-4.5. The concentration of the slurries in the absorbers is about 15%. A relatively large liquid/gas ratio (20-50 gal/1,000scf) is used to prevent scaling.

The pH of the slurry is then adjusted to about 4 to promote oxidation in the following step. If required, a small amount of sulfuric acid, normally less than one ton per 100 tons of inlet SO_2, is added to the slurry for the adjustment. The slurry is then sent to an oxidizing tower where the sulfite and bisulfite are converted to gypsum by air oxidation using rotary atomizers invented by Japan Engineering Consulting Co. (JECCO) at a pressure of 50-57psig and a temperature of 120-180°F. The atomizer is quite effective in producing fine bubbles and is free from scaling, erosion and corrosion. The gas leaving the oxidizer contains some SO_2, and is returned to the absorber. The gypsum is centrifuged. All of the liquor and wash water are used for the gas washing and cooling step. The gypsum grows into large crystals; its moisture content after centrifugation is only 8-10%. The gypsum thus obtained is of high purity and good quality, which make it suitable for use in cement and gypsum board. The gas from the No. 2 absorber is passed through a demister, reheated, and led to a stack. Wash water of the mist eliminator is also used in the system. Normally no wastewater is emitted from the system. More than 90% of SO_2 is recovered.

State of development Four plants are in operation and five others are being constructed or designed as shown in the following table:

User	Plant site	Capacity (scfm)	Absorbent	Number of absorbers	Year of completion
Nippon Kokan	Koyasu	37,000	$Ca(OH)_2$	2	1964
Kansai Electric	Amagasaki	59,000	$Ca(OH)_2$	2	1972
Onahama Smelting	Onahama	54,000	$Ca(OH)_2$	2	1972
Tomakomai Chemical	Tomakomai	35,000	$Ca(OH)_2$	2	1972
Kawasaki Steel	Chiba	71,000	$Ca(OH)_2$	1	1973
Tokyo Electric	Yokosuka	235,000	$CaCO_3$	1	1974
Kansai Electric	Kainan	235,000	$Ca(OH)_2$	1	1974
Tohoku Electric	Hachinoe	224,000	$Ca(OH)_2$	1	1974
Kansai Electric	Kainan	221,000	$Ca(OH)_2$	1	1974

Status of technology Based on extensive studies with a pilot plant, Mitsubishi has succeeded in scale prevention. Scaling can be prevented by the use of a suitable material, shape, and arrangement of the grid in the absorber, by the adjustment of the slurry concentration and pH as well as of the liquid/gas ratio, by the addition of gypsum crystal seed and thorough mixing of lime and the circulating slurry.

The Amagasaki plant has been in continuous operation since its start in April 1972 except for the period of shutdown of the power plant. The desulfurization plant treats a fraction of flue gas 86,000scfm from a 156MW boiler containing about 700ppm SO_2 to recover about 90% of the SO_2. The gas velocity in the absorber is about 11 feet/sec. The pressure drop in the whole system including the cooler, absorbers and demister is 6 in.H_2O. More than 95% of calcium sulfite is oxidized into gypsum in the absorbers due to the low SO_2 concentration; the oxidizing tower is almost unnecessary. The amount of water added to the system is maintained equal to that removed from the system by evaporation in the cooler, by hydration of gypsum, etc. No water is wasted from the plant.

The Onahama plant treats 54,000scfm of gas from a copper smelter containing 20,000-25,000ppm SO_2. More than 99.5% of the SO_2 is recovered with a stoichiometric amount of lime by feeding milk of lime mainly to the No. 2 and partly to the No. 1 absorber. The SO_2 content of the outlet gas is less than 50ppm. The plant came on-stream at the end of October 1972 and has been in continuous operation without trouble except for a period of scheduled shutdown for inspection at the end of November. No scaling was observed at the inspection. The gas supplied from the smelter is a wet gas at 155°F and results in less evaporation of water in the system. Therefore, the amount of water fed to the desulfurization plant slightly exceeds that by evaporation, hydration, etc. A small amount of water is wasted after being treated for pollution control. About 450 tons/day gypsum is produced; three oxidizing towers are provided for the oxidation of calcium sulfite into gypsum; little oxidation occurs in the absorbers due to the high concentration of SO_2.

A one-absorber system will be used for the new plants to save investment cost. To ensure high SO_2 recovery excessive amounts of the absorbents, about 105% of stoichiometric for lime and about 110% for limestone, will be used. For pH adjustment prior to oxidation, a considerable amount of sulfuric acid will be required to convert the excessive absorbent to gypsum. Other facilities and treatments are the same as in the two-absorber system.

In the limestone scrubbing plant in Yokosuka, seawater will be used for cooling flue gas from an oil-fired boiler. The seawater is gradually concentrated in the gas-cooler and therefore should be wasted after being duly treated. Salable gypsum of high purity and good quality will be by-produced using limestone as absorbent.

Economics Investment cost for the Amagasaki plant (59,000scfm) was $1.46 million including various equipment for automatic control and for tests, while that for Tomakomai Chemical (31,000scfm) was $0.32 million. The cost for larger plants (224,000-235,000scfm) is estimated to be $2.6-2.9 million in battery limits. The desulfurization cost for a plant to treat 100,000-150,000scfm gas from an oil-fired boiler is estimated at $0.67-0.88/bl of oil containing 2.5-3.0% sulfur, including depreciation and credit on gypsum at $6/t.

Advantages High recovery of SO_2 is attained and good-quality gypsum is obtained using either lime or limestone without scaling problems. The rotary atomizer is quite effective for oxidation, involving no operational problem. No water is wasted when gas at temperatures above 250°F is treated. Seawater can be used for cooling, although in this case the used seawater should be discharged.

Disadvantage Lime is more expensive than limestone. Although limestone is used for the absorbent, an appreciable amount of sulfuric acid is required to produce gypsum of high purity and good quality. Oversupply of gypsum might occur within several years if too many gypsum-producing desulfurization plants are built.

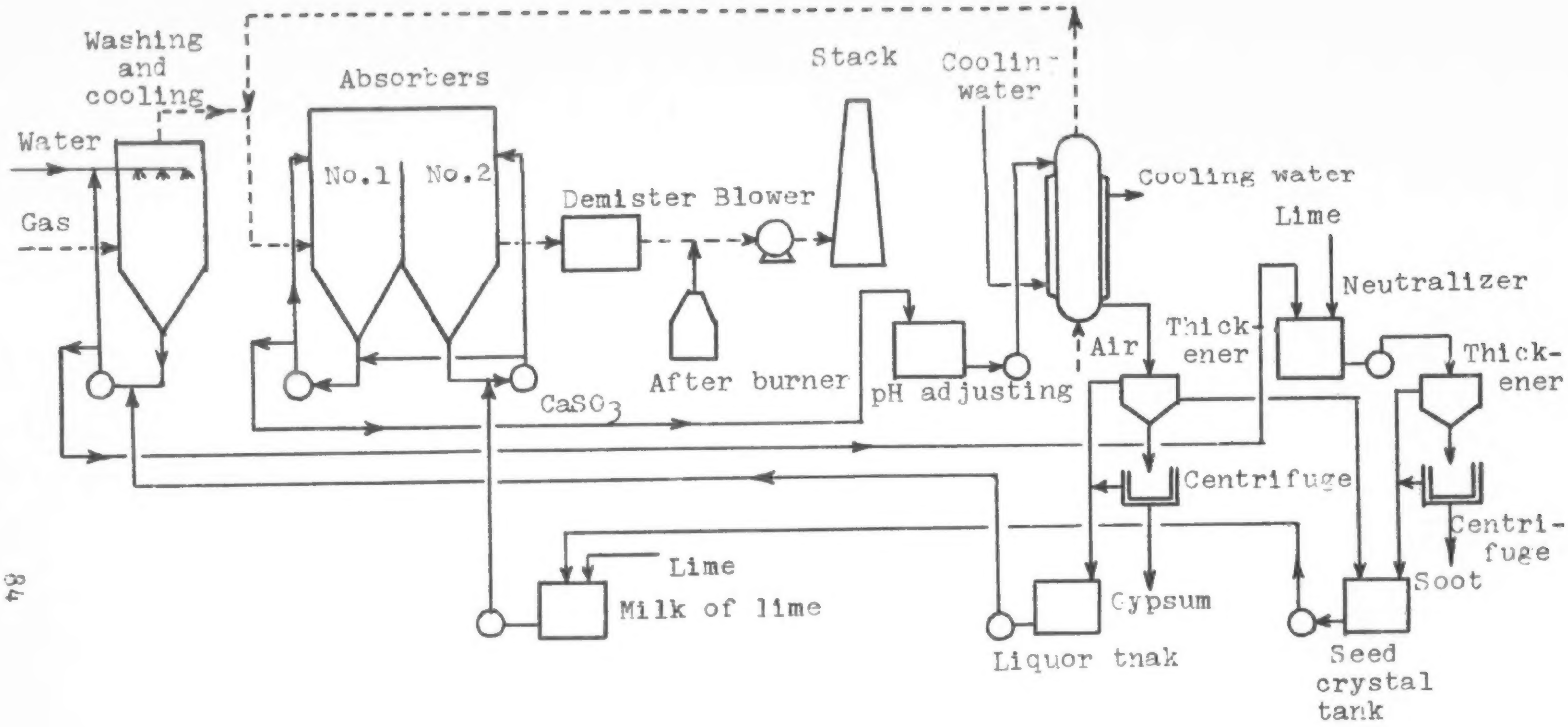

Washing
and
cooling
Water
Gas
Absorbers
No.1
No.2
Demister
Blower
Stack
After burner
$CaSO_3$
Coolin-
water
Cooling water
Air
pH adjusting
Lime
Neutralizer
Thick-
ener
Thick-
ener
Centrifuge
Centri-
fuge
Soot
Gypsum
Lime
Milk of lime
Liquor tnak
Seed
crystal
tank

Figure 6.1.1 Flow sheet of Mitsubishi-JECCO lime-gypsum process

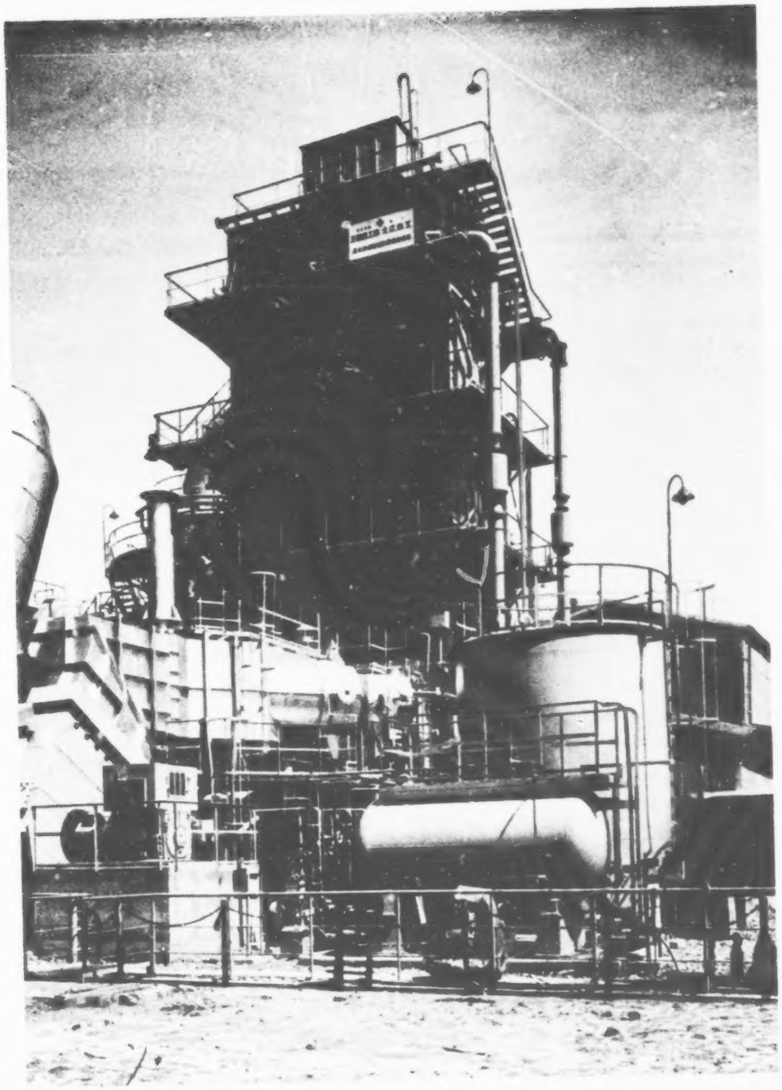


Figure 6.1.2 Amagasaki plant, Kansai Electric Power Co. (Mitsubishi-JECCO process)

6.2 Mitsui-Chemico lime process[7, 8, 10]

Developer Chemico, U.S.A.

Mitsui Aluminum Co. (Miike Power Station), Omuta

Constructor Mitsui Miike Machinery Co. Ltd.
1-1, 2-chome, Muromachi, Nihonbashi, Chuo-ku, Tokyo

Process description Chemico scrubbers (two-stage venturi, Figure 6.2.1) are used for SO_2 and dust removal from flue gas from coal-fired boiler (156MW). Carbide sludge (primarily calcium hydroxide) is used as absorber. Figure 6.2.2 presents a description of the total scrubber system. A photograph of the installation is shown in Figure 6.2.3. The flue gas (302,000scfm) after passing through an electrostatic precipitator contains 0.3 grain/scf of dust and 1,800 to 2,200ppm of SO_2 at 300°F. About 75% of the gas is handled by the scrubber. Two scrubbers were installed but one of them has been used with the other as a back-up., The gas flows down through the first venturi section, up through the mist eliminator section, then passes through the second venturi and mist eliminator sections, is reheated and exhausted to a stack along with the unscrubbed fraction of the gas. Milk of lime is mixed with the discharge from the second venturi; the mixed slurry is partly recycled to the second venturi and partly fed into a delay tank. The slurry in the delay tank is sent to the first-stage venturi. The discharge from the first venturi, consisting mainly of calcium sulfite with small amounts of calcium sulfate, unreacted calcium hydroxide and fly ash, is sent partly to a delay tank and partly to a disposal pond about a mile from the plant. The decanting or settling of the solids takes place there and the supernatant from the pond is recycled to the scrubbing system to prepare milk of lime and also to wash mist eliminators. The outlet gas from the scrubber contains 0,1 grain/scf of dust and 200 to 300ppm of SO_2.

Status of technology The scrubber is 33 feet in diameter and 66 feet high, is constructed of stainless steel, and is lined with glass flake reinforced polyester material. The following operation conditions have been used:

L/G (venturi + spray)	1st stage, 46 to 59 gal/1,000scf
	2nd stage, 42 to 55 gal/1,000scf
Stoichiometry	100 to 105% as pure $Ca(OH)_2$
Percentage solids in slurry	3-5%
Total pressure drop	16 in.H_2O

Prior to the completion of the plant, extensive pilot plant tests were carried out by Mitsui Aluminum Co. leading to the establishment of operation know-how for scale prevention. Precise control of pH to a certain narrow range is important for the scale prevention.

State of development Operation of the commercial plant started in March 1972. After 8 months of satisfactory continuous operation, the plant was subjected to a scheduled shutdown for inspection, which revealed essentially no scaling. Operation was resumed soon and has since been carried out smoothly. The waste disposal pond has a capacity for holding solids discharged over a period of several years. However, to eliminate any possible pollution with sulfite ion in wastewater which could be emitted when the facilities are cleaned in a periodical shutdown of the plant for inspection, some means of converting calcium sulfite to gypsum will be adopted within 1973. Tests have shown that the gypsum can be used for gypsum board and cement although it contains a small amount of fly ash.

Economics The commercial plant cost $3.3 million including two scrubbers. The desulfurization cost is a little less than 1 mil/kWh. About 70% of the desulfurization cost is accounted for by depreciation and interest.

Advantages Stable operation without scale formation is achieved, removing both SO_2 and dust satisfactorily. Carbide sludge, a cheap source of lime, is used. The Chemico scrubber is suited for treating a large amount of gas.

Disadvantage Large amounts of slurry and water must be recycled because of the use of high L/G and low slurry concentration in order to ensure scale prevention.

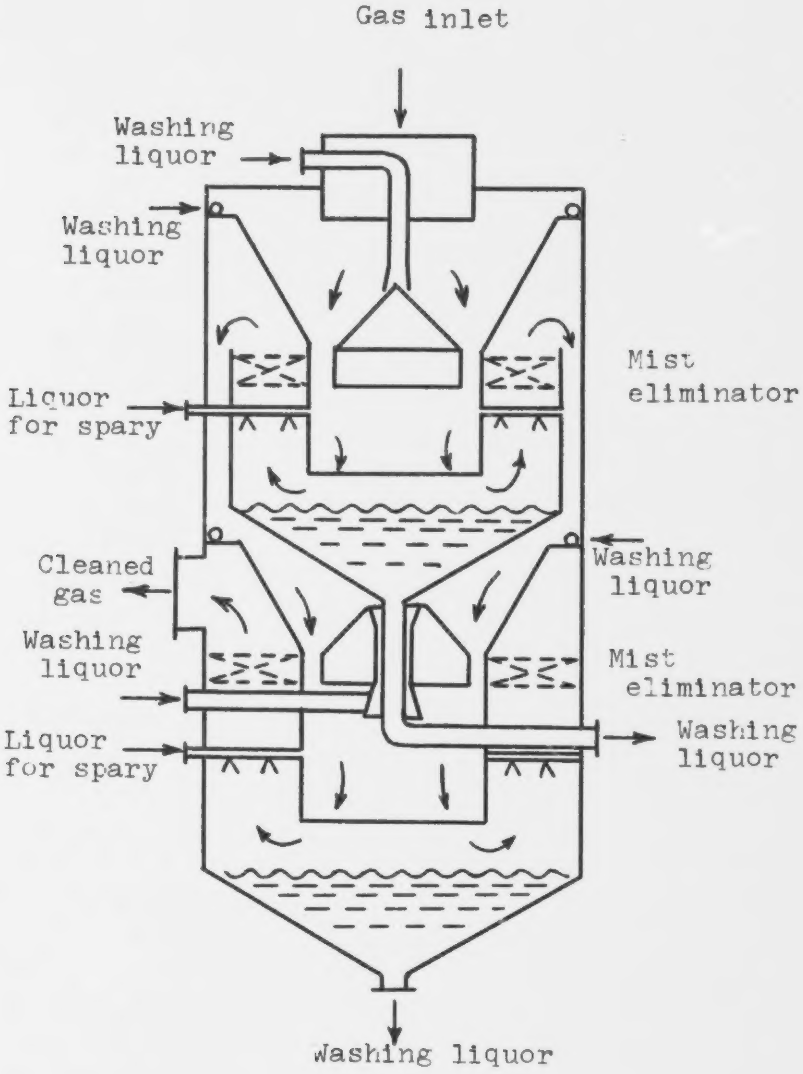
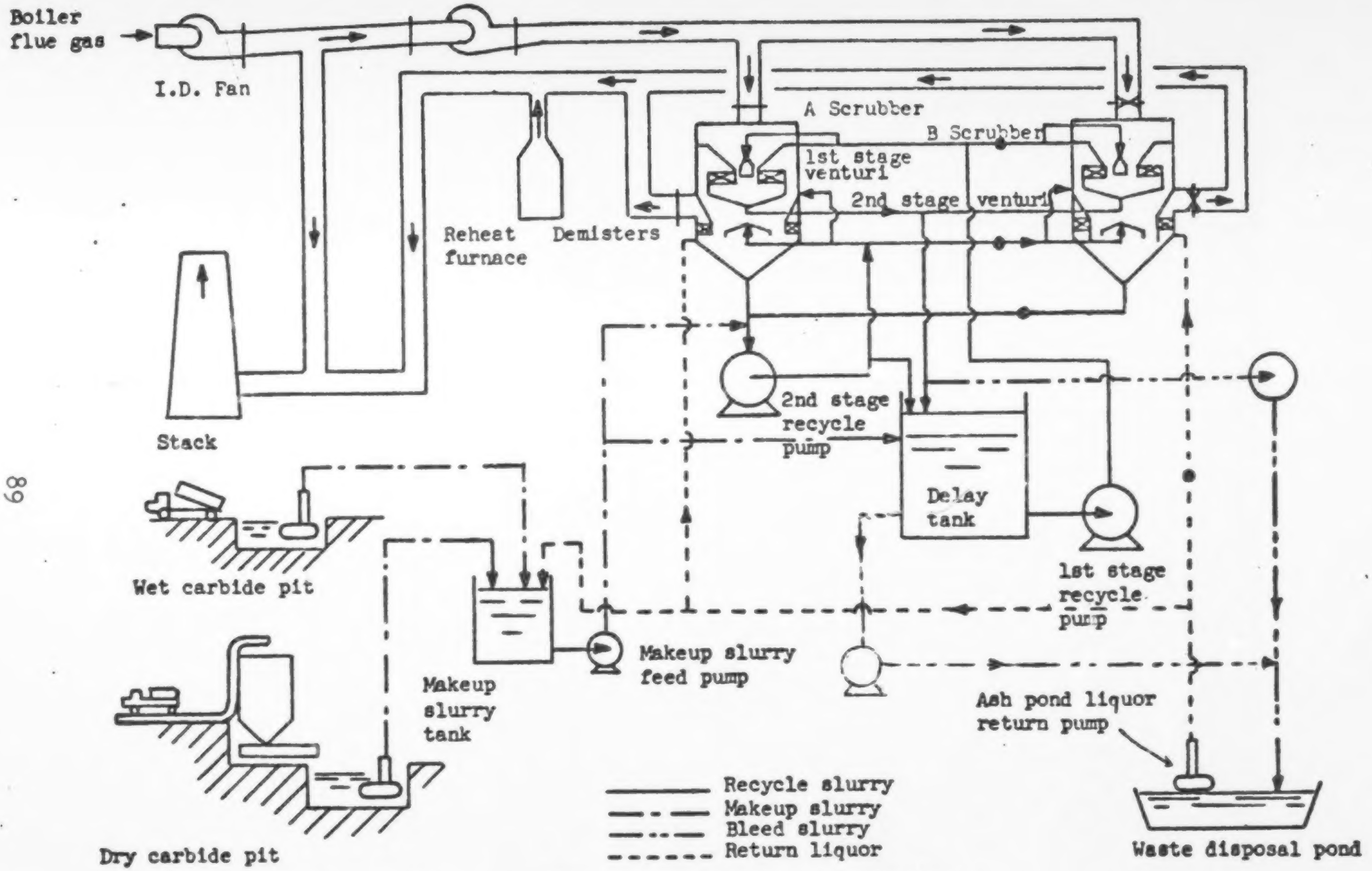

Gas inlet
Washing liquor
Washing liquor
Mist eliminator
Liquor for spary
Cleaned gas
Washing liquor
Washing liquor
Mist eliminator
Liquor for spary
Washing liquor
Washing liquor

Figure 6.2.1 Chemico two-stage venturi scrubber


Boiler flue gas
I.D. Fan
Stack
Reheat furnace
Demisters
A Scrubber
B Scrubber
1st stage venturi
2nd stage venturi
2nd stage recycle pump
Delay tank
1st stage recycle pump
Wet carbide pit
Dry carbide pit
Makeup slurry tank
Makeup slurry feed pump
Ash pond liquor return pump
Waste disposal pond
Recycle slurry
Makeup slurry
Bleed slurry
Return liquor

Note: Only one scrubber system presently in operation.
● indicates a closed valve during 2/72 to 9/72.
⋈ indicates a closed damper during 2/72 to 9/72.

Figure 6.2.2 Mitsui-Chemico lime process

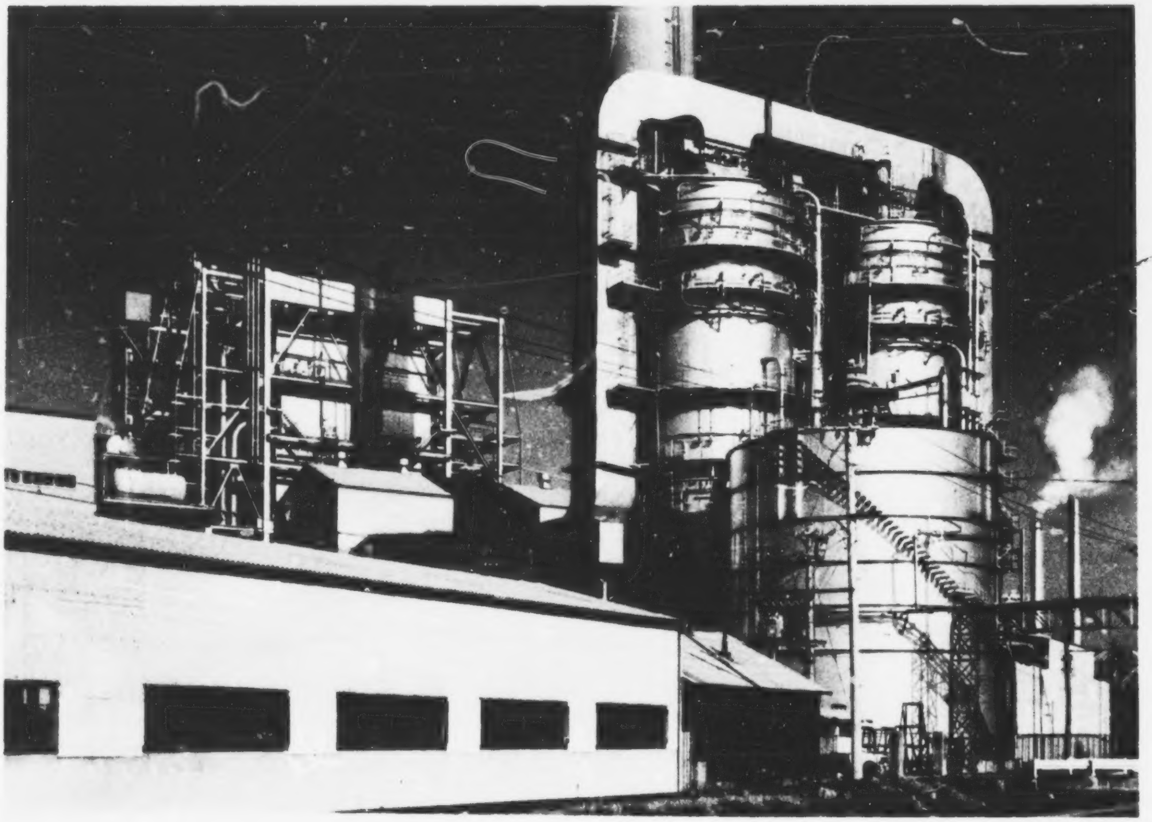


Figure 6.2.3 Omuta plant, Mitsui Aluminum Co.
(Mitsui-Chemico process)

6.3 Babcock-Hitachi limestone-gypsum process

Developer Babcock-Hitachi Co. Ltd.

2-8, Otemachi, Chiyoda-ku, Tokyo

State of development The process is based on a wet-limestone process developed by Babcock and Wilcox, U.S.A. Some modification of the process has been made to produce gypsum with good quality which is salable in Japan. A pilot plant (1,800scfm) has been in operation since late 1972 at the Kure plant of the company. Construction of a prototype plant with a capacity of treating 170,000scfm of flue gas from an oil-fired boiler (100MW equivalent) has been recently started at Mizushima Station of Chugoku Electric Power Co., with commissioning scheduled for late 1973.

Process description A scrubber developed by Babcock and Wilcox is used (Figure 6.3). Flue gas is cooled in a cooling section of the scrubber and led into an absorbing section where SO_2 is reacted with a slurry containing powdered limestone to form calcium sulfite. The desulfurized gas is passed through a demister section, is reheated either by a heat exchanger with steam or by an after-burner, and is emitted. The limestone is finely pulverized by a wet mill, classified and led to a circulation tank, and fed to the scrubber. About 110 to 115% of stoichiometric amount of limestone is used. The slurry reacted with SO_2 is also led into the circulation tank. A portion of the slurry from the circulation tank is continuously sent to a reactor to convert the remaining limestone into gypsum by addition of sulfuric acid and then fed into an oxidizer to convert calcium sulfite to gypsum with air bubbles. The gypsum slurry is led to a thickener and then to centrifuges. Salable gypsum of good quality is obtained. The water from the thickener and centrifuges is returned mainly to the wet mill and partly to the demister for washing. Essentially no wastewater is emitted.

Further modification of the process is planned to increase the desulfurization rate and to reduce the use of excessive limestone and also sulfuric acid.

Advantages Limestone, the cheapest absorbent, is used. Salable gypsum is obtained. Less possibility of scaling than by using lime as the absorbent. Essentially no wastewater is emitted.

Disadvantages A considerable amount of sulfuric acid is required to produce salable gypsum. Limestone should be very finely pulverized to attain high recovery of SO_2.

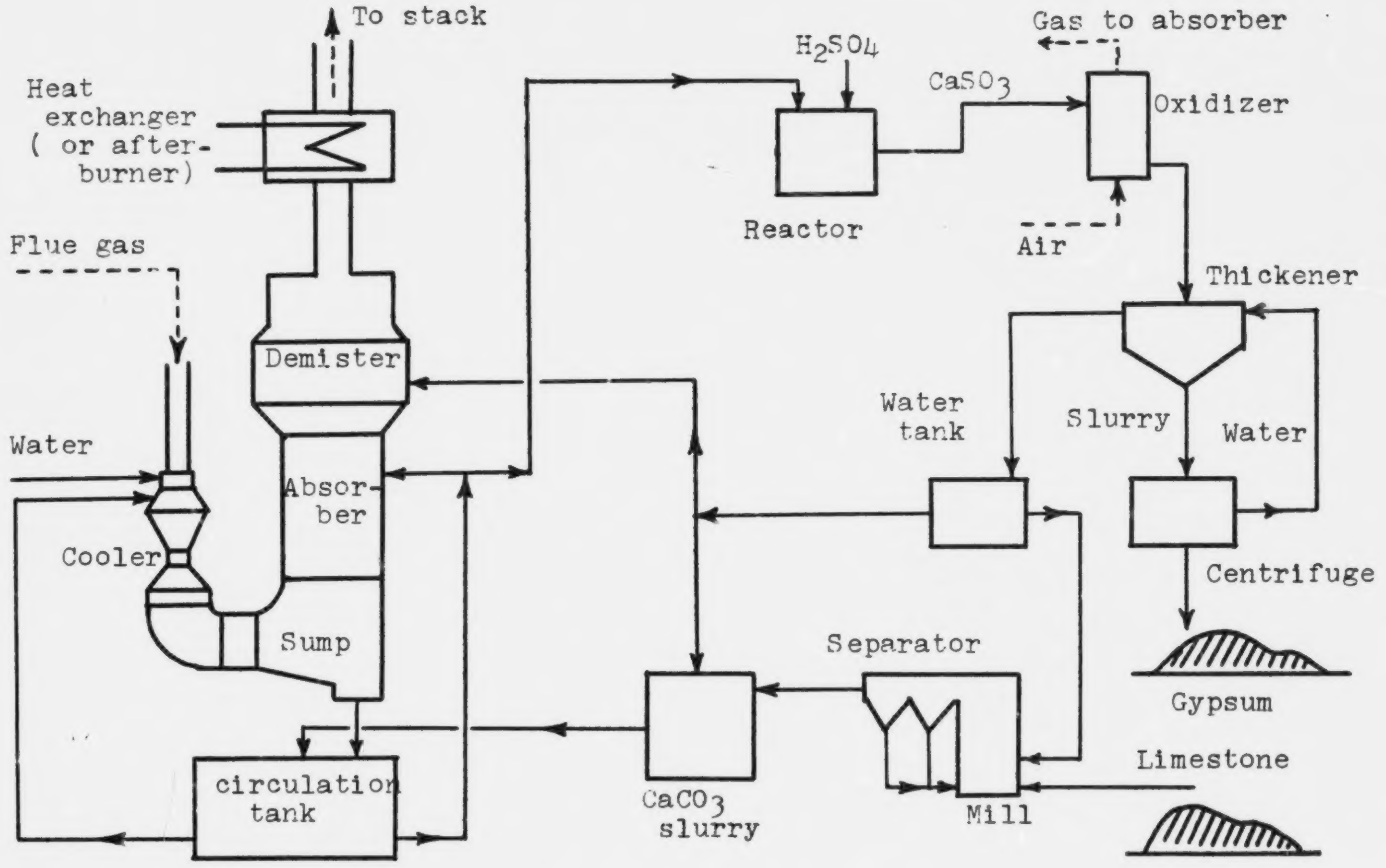

To stack
Heat exchanger (or after-burner)
Flue gas
Water
Cooler
Demister
Absorber
Sump
circulation tank
H_2SO_4
$CaSO_3$
Reactor
Gas to absorber
Oxidizer
Air
Thickener
Water tank
Slurry
Water
Centrifuge
Separator
Gypsum
Limestone
Mill
$CaCO_3$ slurry

Figure 6.3 Flow sheet of Babcock-Hitachi limestone-gypsum process

6.4 IHI-TCA lime gypsum process[7)]

Developer Ishikawajima-Harima Heavy Industries Ltd.
2-2-1, Otemachi, Chiyoda-ku, Tokyo

Process description Turbulent contact absorbers (TCA) with polyethylene balls in three stages are used for the wet-lime process. Flue gas is cooled to below 190°F by a cooler, introduced into one (No. 1) TCA scrubber with water for dust removal, and then into **another** (No. 2) TCA scrubber with milk of lime for desulfurization. The milk of lime is converted mostly **to** calcium sulfite and partly **to** bisulfite removing 90 to 96% of SO_2 in the gas. The slurry from the No. 2 scrubber is put into a recycle tank, mixed with lime, and returned to the No. 2 scrubber. A portion of the circulating slurry is sent to a thickener. The top liquor from the thickener is returned to the recycle tank; the concentrated slurry from the thickener is led into as oxidizer after pH adjustment. Gypsum formed by the oxidation of calcium sulfite is centrifuged. The wash water discharged from the No. 1 TCA scrubber is filtered to remove dust and is recycled. A portion of the filtered water is used for the pH adjustment of the calcium sulfite slurry prior to the oxidation.

State of development A commercial unit with a capacity of treating 61,000scfm of flue gas from a diesel engine generator was installed at Kumagaya plant, Chichibu Cement Co. in 1972. Another unit of equal size is under construction in the same plant. No oxidizer is needed for these plants because a high concentration of oxygen (11 to 12%) and a low concentration of SO_2 (700ppm) result in complete oxidation in the TCA scrubber. Another TCA scrubber for the wet-lime process was installed at Onahama plant, Mitsubishi Metal Co. in 1971 to treat 70,000scfm of waste gas from a copper smelting plant.

Status of technology Low slurry concentration (2%) is used to reduce the erosion of the plastic balls. High L/G ratio (more than 50 gal./1,000scf) is used to prevent scaling. Scaling is apt to occur on the under surface of the grid; therefore, the surface is washed with sprays of slurry from underneath. The gypsum grows into large crystals; its moisture content after centrifugation is 10-15%. The gypsum is used as a retarder of cement setting. A mist eliminator is placed at the upper part of the No. 2 scrubber. Since a high velocity of gas in the scrubber would blow up some of the slurry to the eliminator and cause scaling, the velocity is kept below 10 feet/sec.

Advantage High recovery of SO_2 is attained.

Disadvantages Low slurry concentration and high L/G ratio are required. Use of powdered limestone as an absorbent is difficult because of the wearing of the plastic balls.

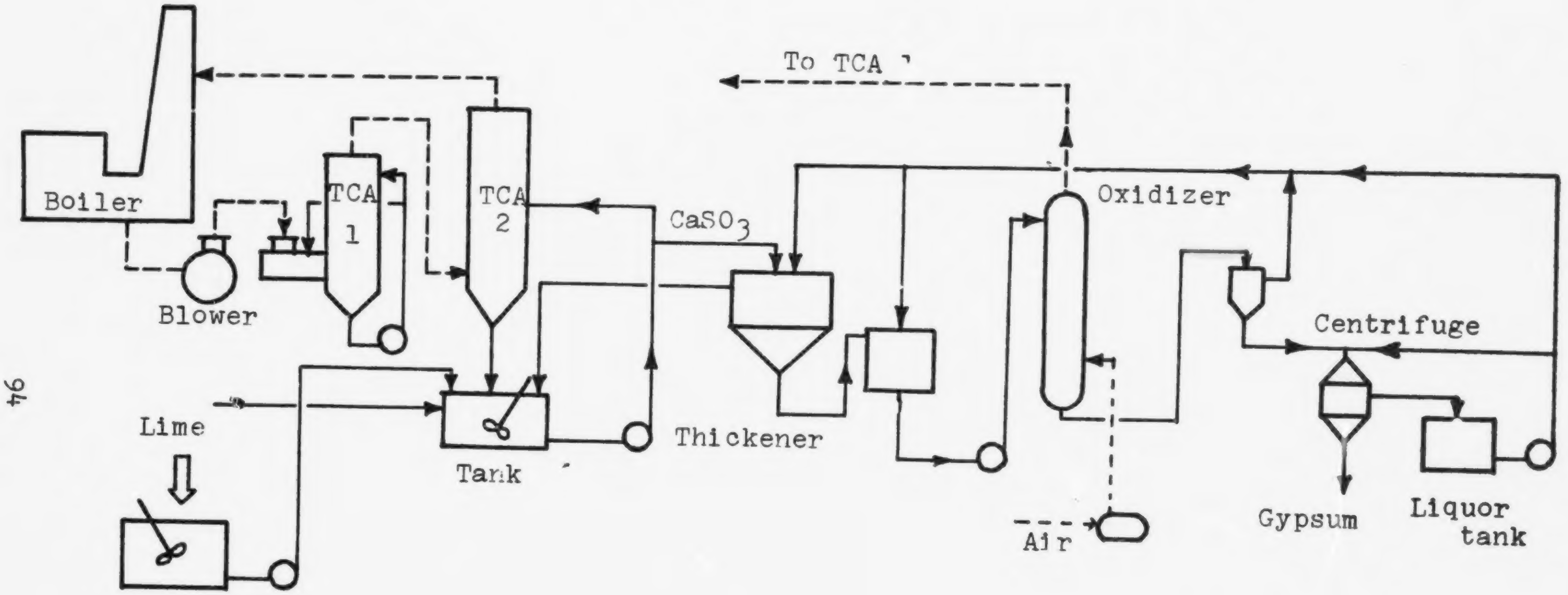

Boiler
Blower
TCA 1
TCA 2
To TCA
$CaSO_3$
Oxidizer
Centrifuge
Lime
Tank
Thickener
Air
Gypsum
Liquor tank

Figure 6.4 IHI-TCA lime-gypsum process

6.5 Other wet-lime processes

6.5.1 Tsukishima-Bahco process

Tsukishima Kikai Co. (17-15, 2-chome, Tsukuda, Chuo-ku, Tokyo) built a wet-lime process plant at Nagoya Factory, Yahagi Iron Co. The plant is designed to treat 47,000scfm waste gas containing 2,000ppm SO_2 from a pelletizing plant of pyrite cinder. A Bahco scrubber and carbide sludge (mainly calcium hydroxide) are used to absorb SO_2. Calcium sulfite thus formed is oxidized with air by an oxidizer developed by Tsukishima. The plant went into operation in December 1971 and encountered some scaling problem, which has nearly been solved.

6.5.2 Mitsui gypsum process

Mitsui Miike Machinery Co. (2-1-1, Muromachi, Nihonbashi, Chuo-ku, Tokyo) has operated a pilot plant with a capacity of treating 1,180scfm of flue gas from a coal-fired boiler with a slurry containing pulverized limestone and a small amount of catalyst which promotes the reaction between SO_2 and limestone and also the oxidation of calcium sulfite into gypsum. The by-produced gypsum has a good quality and can be used for a retarder of cement setting.

6.5.3 Nippon Kokan lime-gypsum process

Nippon Kokan (1-1-1, Marunouchi, Chiyoda-ku, Tokyo) has developed a lime-gypsum process based on several years' experience operating a lime-gypsum process plant at Koyasu built by Mitsubishi Heavy Industries using the Mitsubishi-JECCO process. The Nippon Kokan process resembles the Mitsubishi-JECCO process.

6.5.4 Kawasaki lime process

Kawasaki Heavy Industries (16-1, 2-chome, Nakamachidori, Ikeda-ku, Kobe) is constructing a wet-lime process plant designed to treat 52,900scfm of waste gas from a kraft-recovery boiler at Akita Factory, Jujo Paper Co. Solivore scrubbers (see 7.4) are used. The plant will be completed by May 1973.

7 Other wet processes

7.1 Chiyoda dilute sulfuric acid process (Thoroughbred 101 process)[7,8]

Developer Chiyoda Chemical Engineering & Construction
1580 Tsurumi-cho, Tsurumi-ku, Yokohama

Outline of the process Flue gas is washed with dilute sulfuric acid which contains an iron catalyst and is saturated with oxygen. SO_2 is absorbed and converted to sulfuric acid. Part of the acid is reacted with limestone to produce gypsum. The rest is diluted with gypsum wash water and returned to the absorber.

Description A flow sheet is shown in Figure 7.1.1. Flue gas is first treated by a prescrubber to eliminate dust and to cool the gas to 140°F. The cooled gas is led into a packed tower absorber containing 1 inch Telleretts. Dilute sulfuric acid (2 to 5% H_2SO_4) which contains ferric ion as a catalyst and is nearly saturated with oxygen, is fed to the packed tower. About 90% of SO_2 is absorbed, and partly oxidized into sulfuric acid.

The product acid is led to the oxidizing tower into which air is bubbled from the bottom to complete the oxidation. Most of the acid at 120-150°F nearly saturated with oxygen is returned to the absorber. Part of the acid is treated with powdered limestone (minus 200 mesh) to produce gypsum. A special type of crystallizer has been developed to obtain good crystalline gypsum 100 to 300 microns in size. The gypsum is centrifuged from the mother liquor and washed with water. The product gypsum is of good quality and salable.

The mother liquor and wash water are sent to the scrubber. The amount of input water--wash water and the water to the prescrubber--is kept equal to the amount of water lost by evaporation in the scrubbers and by hydration of gypsum. No wastewater is emitted.

State of development The operation of a pilot plant (6,000scfm) has led to the construction of the following commercial plants:

Table 7.1.1 Commercial plants by Chiyoda process

User	Plant site	Source of gas	Size, scfm	Completion
Nippon Mining	Mizushima	Claus furnace	20,600	October 1972
Fuji Kosan	Kainan	Oil-fired boiler	94,100	October 1972
Mitsubishi Rayon	Otake	Oil-fired boiler	52,900	December 1973
Tohoku Oil	Sendai	Claus furnace	8,200	January 1973
Daicel Ltd.	Aboshi	Oil-fired boiler	59,000	October 1973
Hokuriku Electric	Shinminato	Oil-fired boiler	442,000	June 1974
Mitsubishi Petrochem.	Yokkaichi	Oil-fired boiler	413,000	December 1974

Status of technology The iron catalyst is less reactive at low temperature but is as reactive as manganese catalyst at operation temperatures above 120°F (Figure 7.1.2). It is not poisoned by impurities in the gas, even when flue gas from a coal-fired boiler is used. Catalyst loss is very small (Figure 7.1.3). The towers of the commercial plants are provided with rubber or FRP linings. Stainless steel is also usable; the ferric catalyst works also as a corrosion inhibitor.

A large L/G ratio is required to attain high SO_2 recovery as shown in Figure 7.1.4; large pumps and fairly large absorber and oxidizer are required as shown in the following table.

Table 7.1.2 Size of towers (feet)

	Absorber		Oxidizer	
Capacity (scfm)	Diameter	Height	Diameter	Height
117,600	29.7	49.5	13.4	62.7
294,100	49.5	49.5	21.1	62.7

A double-cylinder type reactor (Figure 7.1.5) including an oxidizing section in the center and a scrubbing section in the outer part has been developed recently instead of using two towers. The absorbing liquor goes down the scrubbing section, then goes up in the oxidizing section and overflows to the scrubbing section. The reactor enables some savings to be made in floor space and investment cost.

Advantages The process is simple and the plant is easy to operate. Even in the event that the gypsum-producing system has to be stopped for a day or two for repairs, the absorbing system can be operated continuously. The concentration of sulfuric acid increases by 1 or 2% in this case but SO_2 recovery is not decreased. Catalyst is cheap and is not poisoned by impurities in the gas. Salable gypsum of good quality is obtained from limestone without scaling problems.

Disadvantage Large pumps and a fairly large scrubber and oxidizer are required. A large L/G is required when SO_2 concentration of inlet gas is high.

Table 7.1.3 Cost estimation* ($1 = ¥308)

(Inlet gas SO_2 1,000ppm, dust 0.08 grain/scf)
(Outlet gas SO_2 100ppm, dust 0.04 grain/scf)

	Capacity		
	800MW (1.51×10^6 scfm)	500MW (0.95×10^6 scfm)	250MW (0.475×10^6 scfm)
Plant cost ($) (A)	17.2×10^6	12.5×10^6	7.0×10^6
Fixed cost ($/year) (B)	3.10×10^6	2.25×10^6	1.26×10^6
Direct cost ($/year)			
Limestone (0.25¢/lb)	430,000	272,000	135,600
Electricity (0.7¢/kWh)	789,000	529,000	308,000
Water (8¢/1,000 gal.)	25,400	17,000	8,400
Fuel oil ($3.18/bl)	1,035,400	648,700	325,600
Steam (0.12¢/lb)	39,700	25,100	12,600
Catalyst (6¢/lb)	11,000	8,000	4,000
Labor ($12,000/year/capita)	144,000	96,000	96,000
Maintenance	344,000	250,000	140,000
Subtotal (C)	2,818,500	1,845,800	1,030,200
Net running cost (B + C = D)	5,918,500	4,095,800	2,290,200
Overhead (E) (12% of C)	338,200	221,500	123,600
Running cost (D + E)	6,256,700	4,317,300	2,413,800
Desulfurization cost without by-product credit ($/bl)	0.645	0.712	0.797
Desulfurization cost without by-product credit ($/MWhr)	0.992	1.095	1.225

* Estimation made by Chiyoda in February 1973

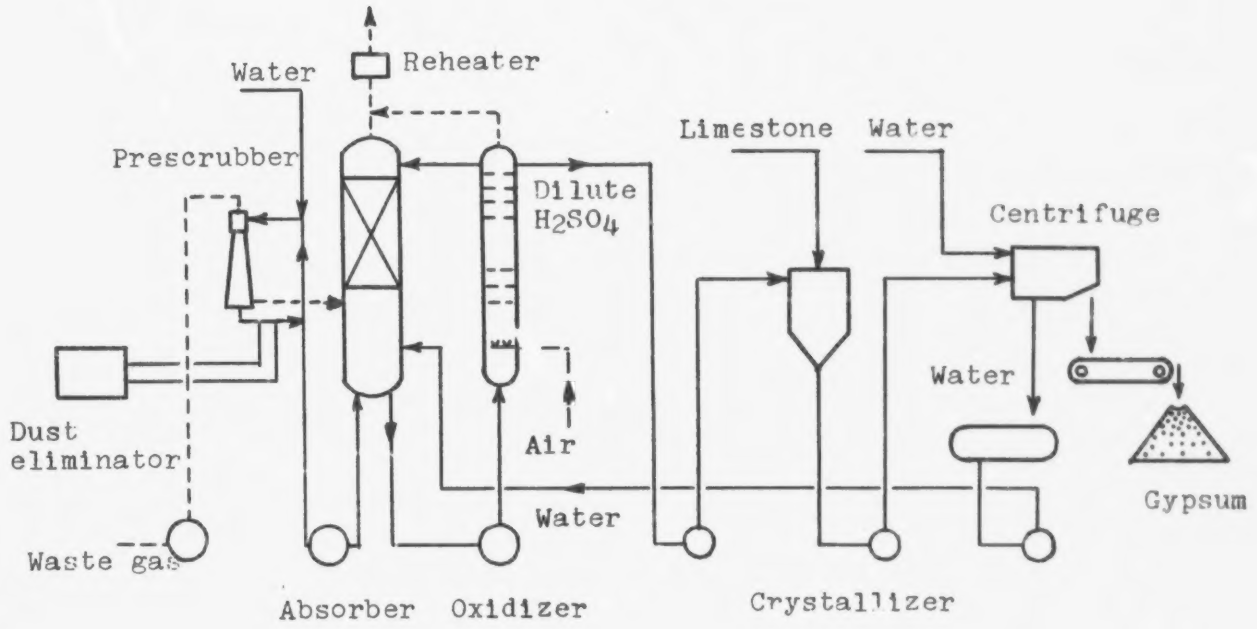

Water
Reheater
Prescrubber
Dilute
H_2SO_4
Limestone
Water
Centrifuge
Dust
eliminator
Air
Water
Water
Gypsum
Waste gas
Absorber
Oxidizer
Crystallizer

Figure 7.1.1 Flow sheet of Chiyoda Thoroughbred 101 process

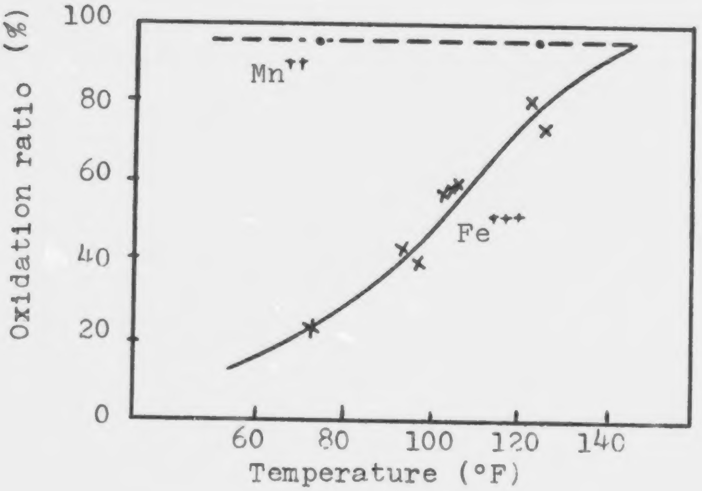


Figure 7.1.2 Temperature and oxidation ratio with catalysts

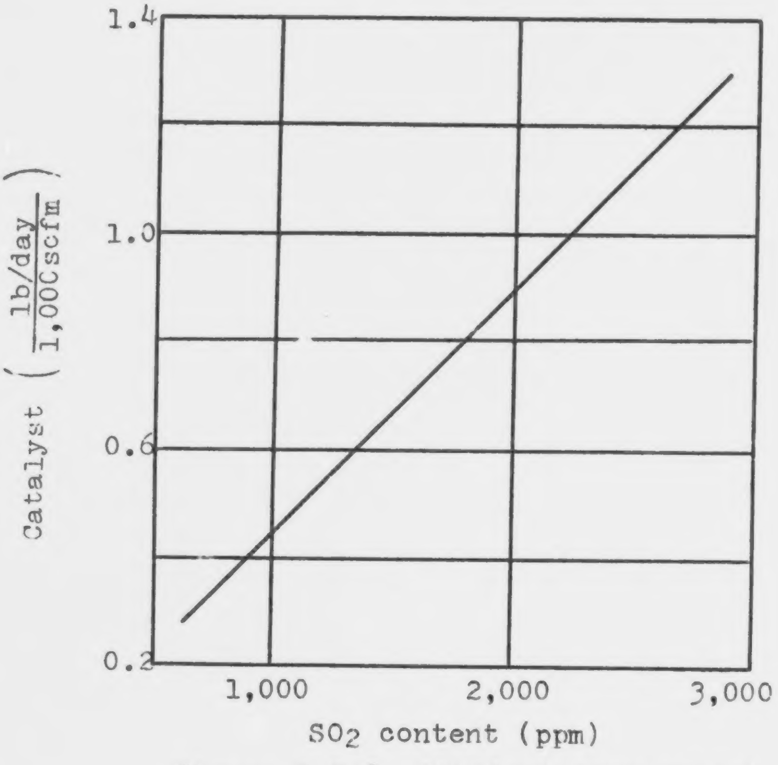


Figure 7.1.3 Catalyst requirement

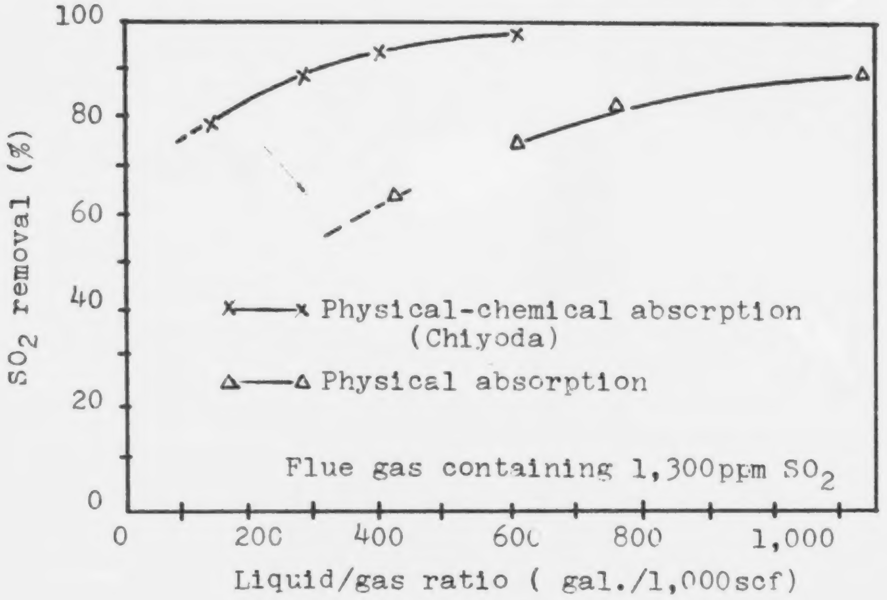


Figure 7.1.4 Liquid/gas ratio and SO_2 removal

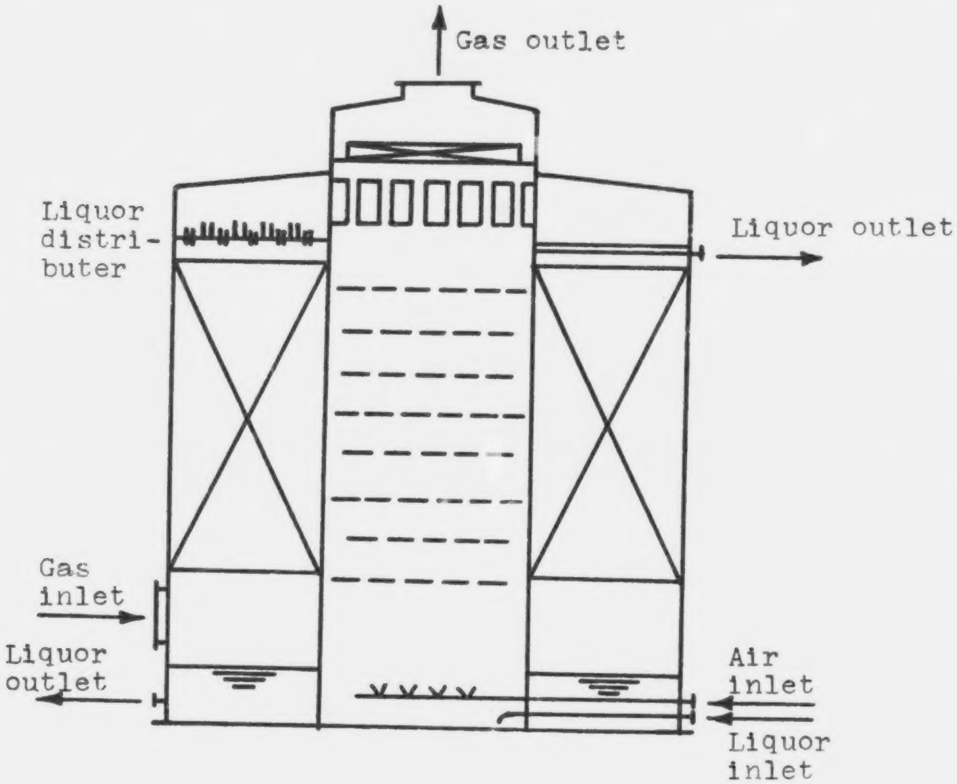

Gas outlet
Liquor distri-buter
Liquor outlet
Gas inlet
Liquor outlet
Air inlet
Liquor inlet

Figure 7.1.5 Double-cylinder type reactor

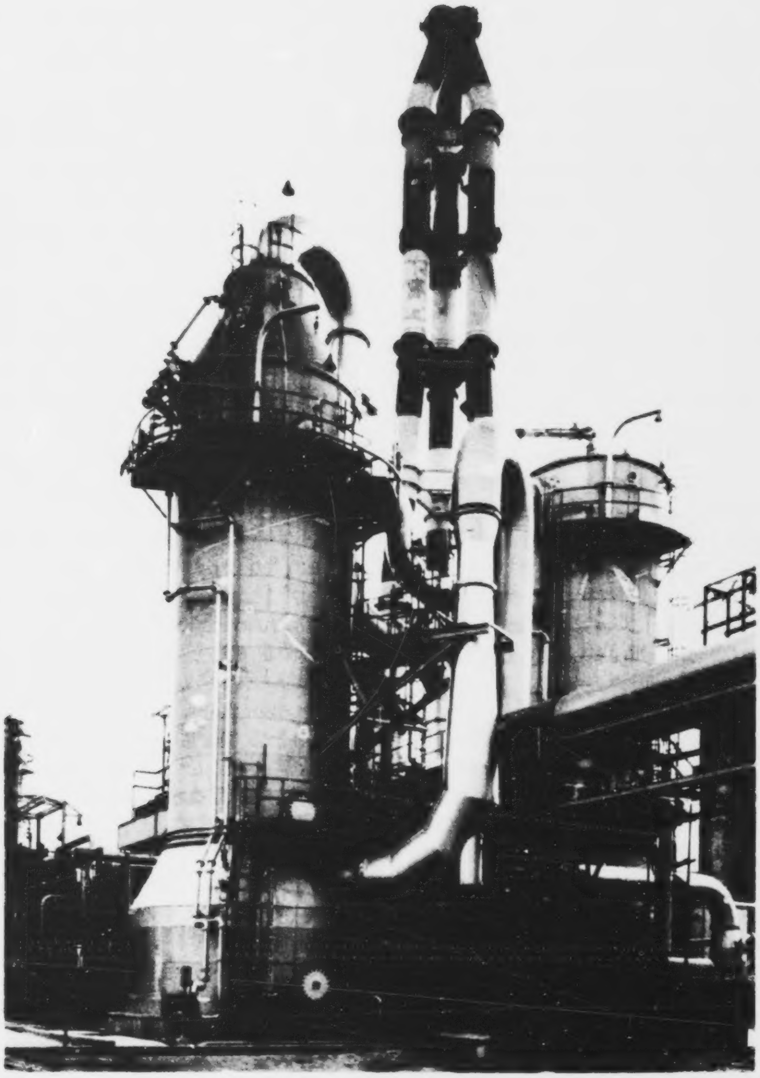


Figure 7.1.6 Mizushima plant, Nippon Mining

(Chiyoda process)

7.2 Mitsui Mining magnesium process (Hibi process)11)

Developer Mitsui Mining and Smelting Co. Ltd.
1-1, 2-chome, Muromachi, Nihonbashi, Chuo-ku, Tokyo

Process description The Hibi process features absorption of SO_2 by magnesium hydroxide slurry in a special cross-flow type absorber developed by Mitsui Mining and Smelting Co. Magnesium sulfite formed by the reaction is calcined to regenerate SO_2 and MgO. The recovered SO_2 is used for sulfuric acid production. A flow sheet of the process is shown in Figure 7.2. The absorber consists of an empty chamber with two rotating shafts with many spoons. Magnesium sulfite slurry (concentration 10%, pH 7) is charged onto the rotating spoons and sprinkled in small particles in the chamber. Two absorbers, 12 feet wide, 14 feet long and 16 feet high are used in series to treat 53,000scfm of gas (47,000scfm tail gas of sulfuric acid plant and 6,000scfm gas from a dryer). The SO_2 concentration of the inlet gas ranges from 1,500 to 2,000ppm and that of outlet gas from 100 to 200ppm. Pressure drop by the absorber is only 0.4 in. H_2O. L/G of about 15 gal./1,000scf is used. Magnesium bisulfite is formed in the slurry, which is then reacted with magnesium hydroxide to form magnesium sulfite. A large portion of the slurry is recycled to the absorber. The rest of the slurry is centrifuged to separate crystalline magnesium sulfite $MgSO_3 \cdot 6H_2O$ from a liquor containing magnesium sulfate formed by oxidation of the sulfite; about 7 to 10% of the sulfite is oxidized during the absorption step.

The solid sulfite is then dried in a rotary dryer by hot gas to convert $MgSO_3 \cdot 6H_2O$ into $MgSO_3 \cdot H_2O$. The gas from the dryer (6,000scfm) contains some SO_2 and is returned to the absorber. The dryer discharge is then decomposed into MgO, SO_2 and H_2O by indirect heating to 1,300 to 1,380°F in a kiln made of a special heat-resistant alloy. The gas from the kiln contains 10 to 20% SO_2 and is returned to the sulfuric acid plant. About 7 to 10% of magnesium sulfite charged is oxidized into sulfate during the heating steps. The discharge from the kiln, consisting of MgO with a small amount of $MgSO_4$, is returned to the absorption step. The magnesium sulfate solution from the centrifuge is concentrated in a vacuum crystallizer to obtain crystalline $MgSO_4 \cdot 7H_2O$ which is centrifuged and used for fertilizer and other uses.

State of development A commercial plant with a capacity of treating 47,000scfm tail gas from a sulfuric acid plant has been on-stream since October 1971.

Advantages The absorber has little possibility of scaling because of the simple structure. The operation is not hindered even when scaling occurs. Indirect heating of the sulfite gives concentrated SO_2 gas suitable for sulfuric acid production.

Disadvantages The size of the absorber is limited because the rotating shaft more than 12 feet long would cause mechanical trouble during the operation. It is not easy to treat more than 60,000scfm of gas in one absorber with SO_2 recovery higher than 90%. Demand for magnesium sulfate is limited.

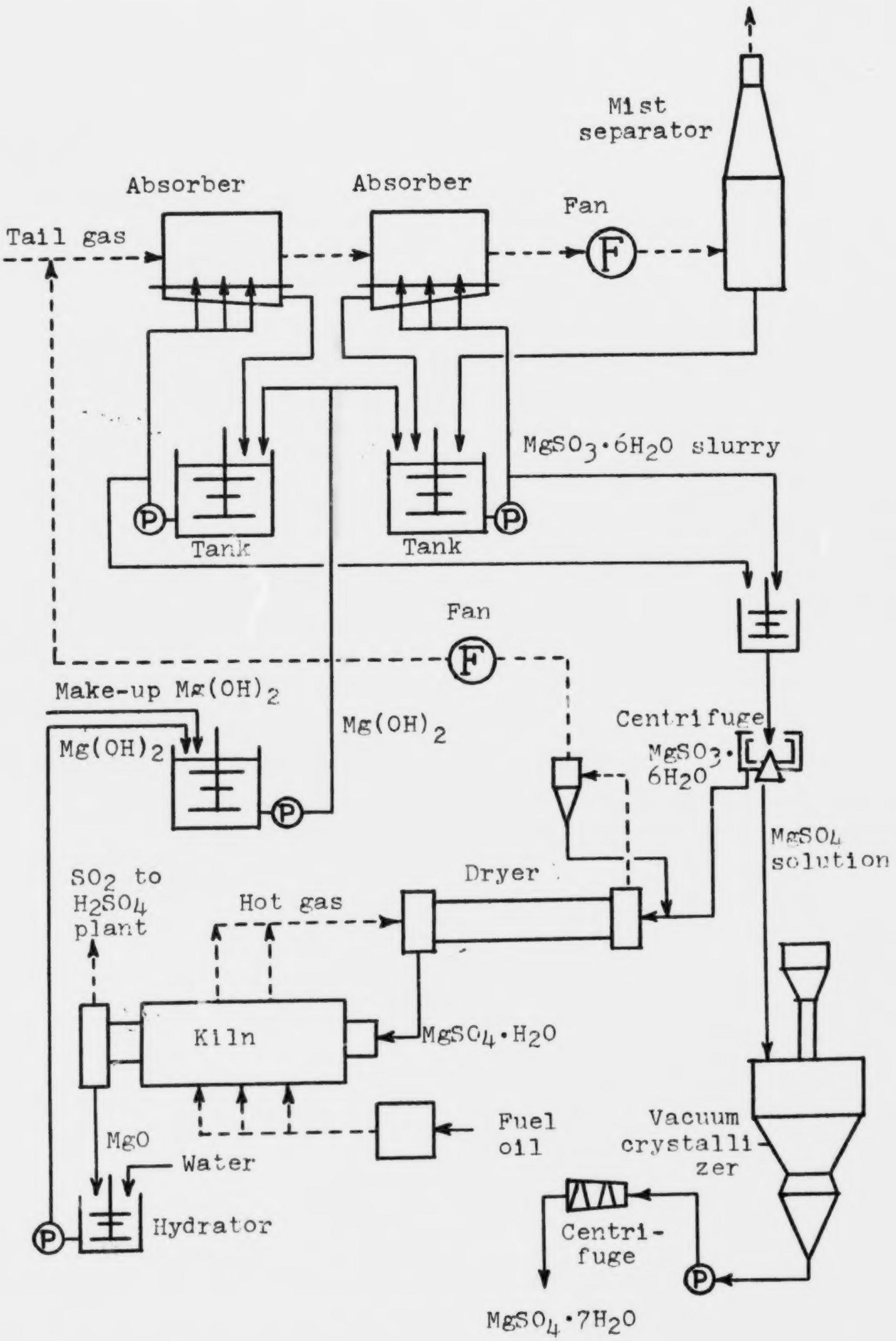

Mist separator
Absorber
Absorber
Fan
Tail gas
$MgSO_3 \cdot 6H_2O$ slurry
Tank
Tank
Fan
Make-up $Mg(OH)_2$
$Mg(OH)_2$
$Mg(OH)_2$
Centrifuge
$MgSO_3 \cdot 6H_2O$
$MgSO_4$ solution
SO_2 to H_2SO_4 plant
Hot gas
Dryer
Kiln
$MgSO_4 \cdot H_2O$
Fuel oil
Vacuum crystallizer
MgO
Water
Hydrator
Centrifuge
$MgSO_4 \cdot 7H_2O$

Figure 7.2 Flow sheet of Mitsui Mining magnesium process

7.3 Onahama magnesium process

Developer Onahama Smelting and Refining Co. Ltd.
5-2, 1-chome, Otemachi, Chiyoda-ku, Tokyo

Tsukishima Kikai Co.
17-15, 2-chome, Tsukuda, Chuo-ku, Tokyo

Process description Waste gas from a copper smelting plant (53,000scfm containing 15,000-25,000 ppm SO_2) after passing through an electrostatic precipitator and a cooler is treated by an absorber 13.2ft in diameter and 89ft in height with a magnesium hydroxide slurry. Magnesium sulfite is formed by absorbing more than 99.5% of the SO_2, centrifuged, dried in a dryer 10ft in diameter and 83ft in length, and then decomposed in a rotary kiln 11.2ft in diameter and 172ft in length using carbon and fuel. The decomposition produces magnesium oxide and a gas containing 13-15% SO_2. The former is returned to the absorbing step after being slaked; the latter is used for production of concentrated sulfuric acid at a rate of 6,600t/month. As the gas contains much SO_2 and less oxygen, the oxidation of magnesium sulfite into sulfate in the absorbing step is virtually none.

State of development A commercial plant has been in operation since December 1972.

Advantage High recovery of SO_2.

Disadvantage When the process is applied for the treatment of flue gas, some oxidation will occur in the absorbing step requiring the treatment of the water-soluble magnesium sulfate.

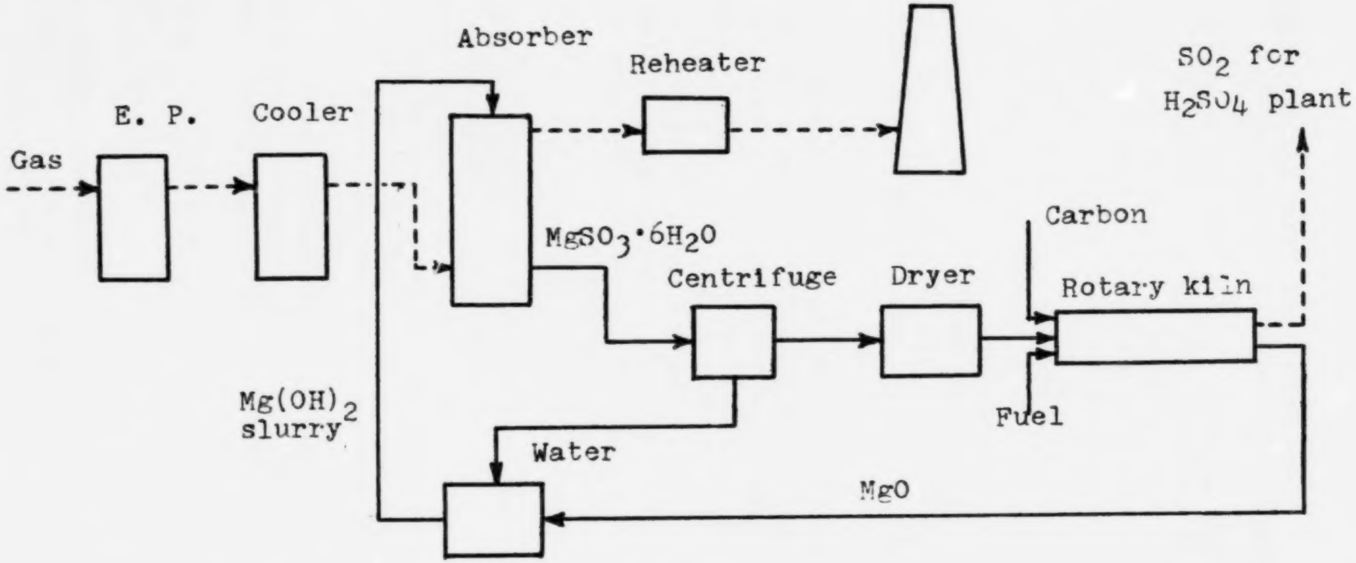

Gas
E. P.
Cooler
Absorber
Reheater
SO_2 for
H_2SO_4 plant
$MgSO_3 \cdot 6H_2O$
Centrifuge
Dryer
Carbon
Rotary kiln
Fuel
$Mg(OH)_2$ slurry
Water
MgO

Figure 7.3 Simplified flow sheet of Onahama magnesium process

7.4 Kawasaki magnesium process7)

Developer Kawasaki Heavy Industries Ltd.
16-1, 2-chome, Nakamachidori, Ikeda-ku, Kobe

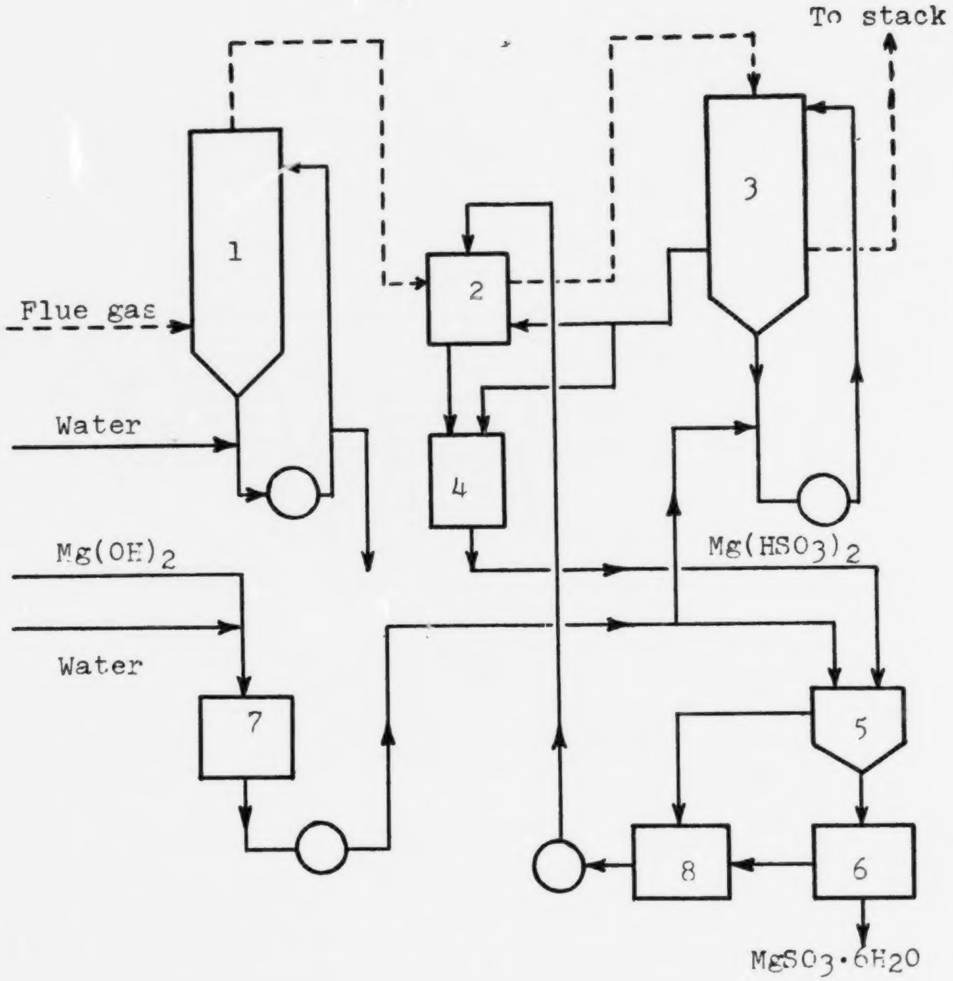
Process description The process features the use of magnesium hydroxide obtained from seawater as an absorbent and two-stage absorbers to obtain large filterable crystals of magnesium sulfite (Figure 7.4.1). Flue gas is first cooled in a scrubber and led into the first absorber and then the second absorber. A magnesium hydroxide slurry (about 5% solid) is fed into the second absorber to form magnesium sulfite, which is then led into the first absorber to form magnesium bisulfite. The bisulfite is reacted with magnesium hydroxide in a crystallizer to produce magnesium sulfite $MgSO_3 \cdot 6H_2O$ in large crystals with an average size of about 300 microns. The sulfite is easily centrifuged; moisture content of the centrifuge discharge is only about 7%. The sulfite can be calcined to release SO_2 and to produce magnesium oxide which is used for the absorption of SO_2.

Solivore type scrubber and absorbers are used (Figures 7.4.2 and 7.4.3). In the scrubber, water is sprayed before and after a venturi. Adiabatic expansion occurs as the gas passes through the venturi, resulting in a lowering of temperature and condensing of moisture on the surface of dust particles. The particles of dust readily stick together to form larger particles which are removed easily. In the absorbers the slurries are sprayed through a special type of nozzles. About 90% of dust and 95% of SO_2 are removed. Pressure drop is low with the Solivore scrubber. For example, the drop is 4-5 in.H_2O with a Solivore scrubber as compared with 28-32 in.H_2O for usual venturi scrubbers.

State of development A pilot plant of the absorption step with a capacity of treating 2,900scfm of flue gas from an oil-fired boiler has been in operation. Bench-scale tests on the calcination step was also made. There is no plan yet to construct a commercial plant including the calcination step. But it is likely that Kawasaki will build a commercial plant using the scrubbing step followed by the oxidation step of magnesium sulfite to produce a waste magnesium sulfate solution. Using the Solivore scrubbers, Kawasaki has recently constructed three commercial plants based on the sodium process and is constructing a commercial plant based on the lime process (see 5.13.4 and 6.5.4).

Advantages The Solivore scrubber is highly effective for the removal of both dust and SO_2 with a low pressure drop. Filterable magnesium sulfite is obtained.

Disadvantages The structure of the Solivore scrubber is not simple; the scrubber could be more expensive than usual venturi scrubbers and might have some possibility of scaling when lime is used as the absorbent.


To stack
3
1
2
Flue gas
Water
4
Mg(OH)$_2$
Mg(HSO$_3$)$_2$
Water
7
5
8
6
MgSO$_3$·6H$_2$O

1: Prescrubber
2: No.1 absorber
3: No.2 absorber
4: Crystallizer
5: Separator
6: Centrifuge
7: Tank
8: Mother liquor tank

Figure 7.4.1 Kawasaki magnesium process

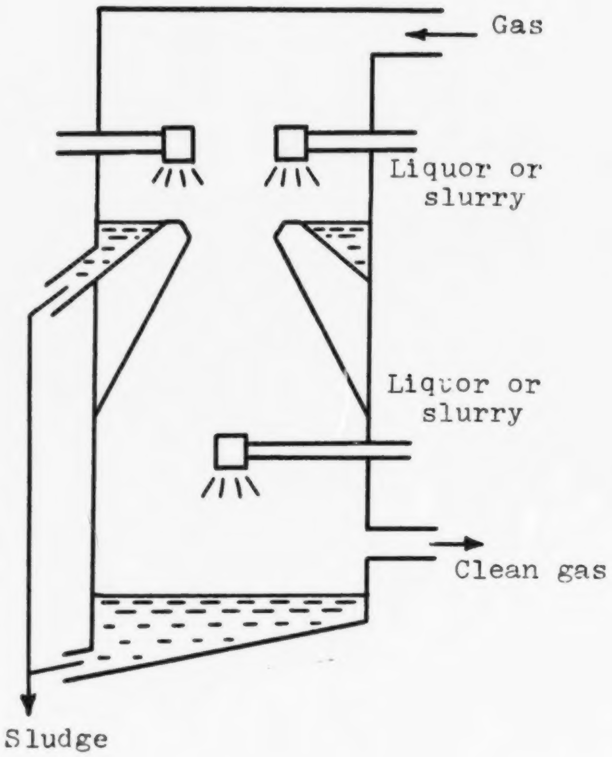

Gas
Liquor or slurry
Liquor or slurry
Clean gas
Sludge

Figure 7.4.2 Solivore scrubber

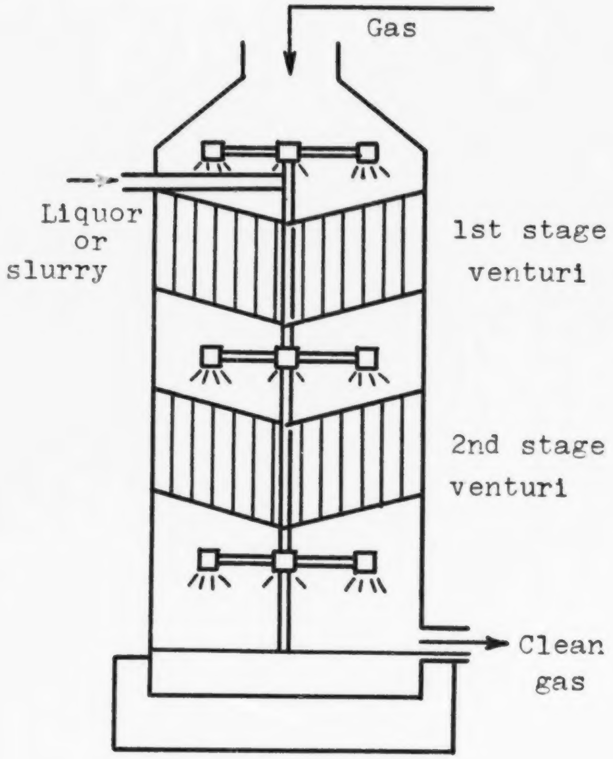

Gas
Liquor or slurry
1st stage venturi
2nd stage venturi
Clean gas

Figure 7.4.3 Two-stage multi Solivore scrubber

7.5 Mitsui-Grillo magnesium-manganese process[7, 8]

Developer Grillo Werke, West Germany
Mitsui Shipbuilding Co.
5-6-4, Tsukiji, Chuo-ku, Tokyo

Process description Flue gas is first cooled in a cooler with water sprays and then desulfurized in a spray tower with a slurry containing magnesium and manganese oxides. Sulfites and sulfates of both magnesium and manganese are formed which are then dried in a spray dryer at about 660°F. The dried product is reacted in a fluidized bed roaster at about 1,700°F with a reducing gas formed by combustion of oil to release SO_2 and to regenerate magnesium and manganese oxides. The gas leaving the roaster containing 7-9% SO_2 is passed through a cyclone, boiler, heat exchanger, and an electrostatic precipitator, and used for sulfuric acid production. More than 90% of SO_2 in the flue gas is recovered. The presence of manganese promotes the desulfurization, oxidation of magnesium sulfite into sulfate, and also the decomposition of magnesium sulfate by the roasting.

State of development Mitsui was licensed by Grillo to use the absorption step, developed the regeneration step including the roaster, and built a pilot plant. The capacity of the pilot plant is 700scfm for the absorption step and equivalent to 3,000scfm for the regeneration step; operation of the roaster has been carried out intermittently.

Status of technology The operating conditions for the absorption step is as follows: gas velocity in the absorber, 36ft/sec; L/G, 14 gal/1,000scf; solids concentration, 30%; pH of recirculating slurry, 6-7. The presence of manganese eliminates the need for a reducing agent in the roasting step as in the Chemico process.

Advantages High recovery of SO_2 is attained with a relatively small scrubber absorber. Manganese promotes the decomposition of the sulfates.

Disadvantages A large dryer is required. The SO_2 concentration of the gas for sulfuric acid plant is not high.

Economics The estimated investment and desulfurization costs for commercial plants with various capacities are listed below.

	Capacity (1,000scfm)			
	118	353	589	1,177
Investment cost (millions of dollars)	3.08	7.46	11.36	20.77
Desulfurization cost* (\$/bl oil)	1.01	0.78	0.73	0.65

* including depreciation (14.3% a year) and credit for sulfuric acid (\$14.6/t).

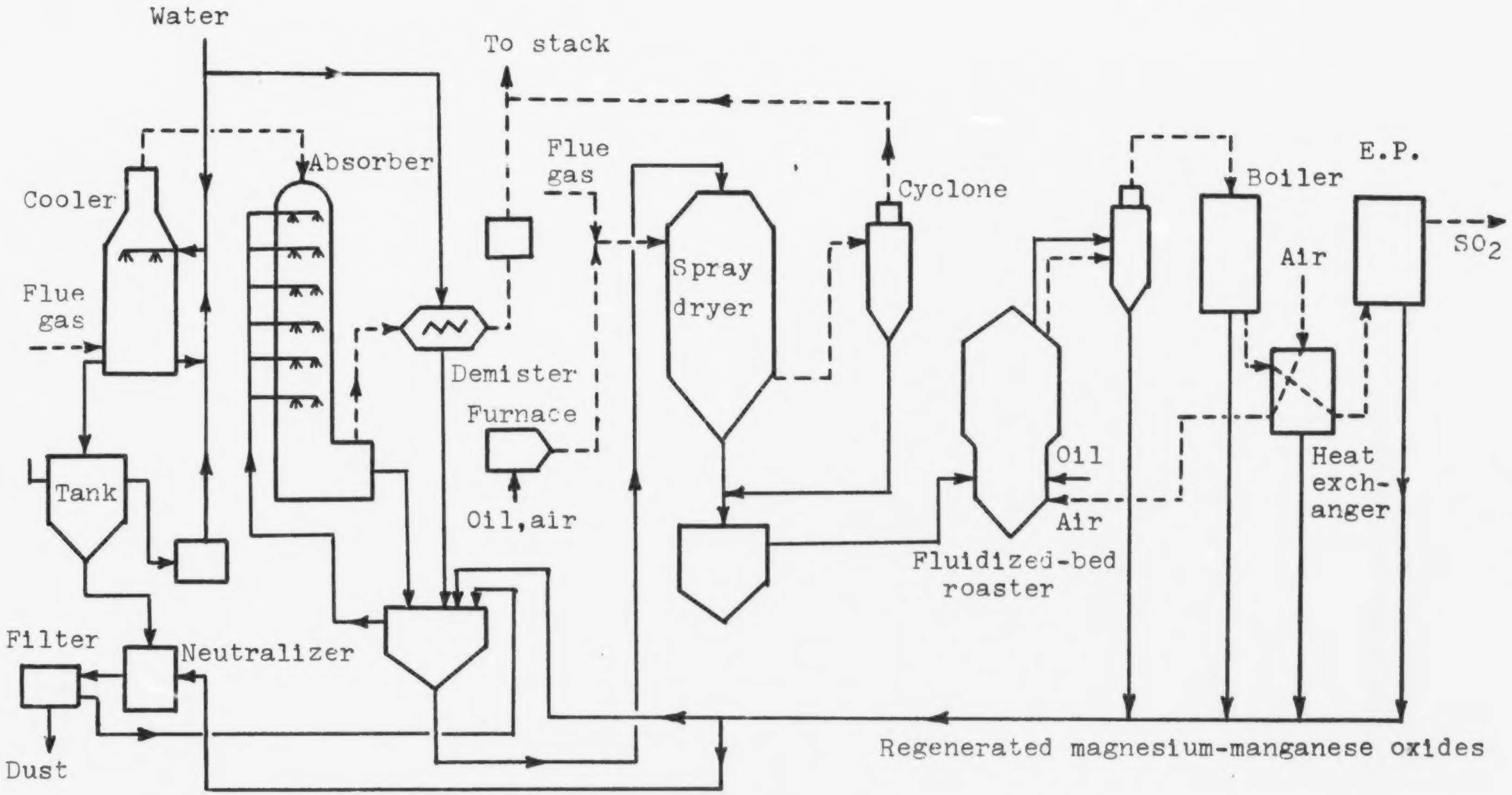

Water
To stack
Flue gas
Absorber
Cooler
Flue gas
Demister
Furnace
Oil,air
Tank
Filter
Neutralizer
Dust
Spray dryer
Cyclone
Boiler
E.P.
SO$_2$
Air
Oil
Air
Heat exch-anger
Fluidized-bed roaster
Regenerated magnesium-manganese oxides

Figure 7.5 Flow sheet of Mitsui-Grillo process

7.6 . Chemico-Mitsui magnesium process

Developer Chemico, U.S.A.

Constructor Mitsui Miike Machinery Co.
2-1-1, Muromachi, Nihonbashi, Chuo-ku, Tokyo

Process description SO_2 in waste gas is absorbed with magnesium hydroxide slurry to form magnesium sulfite. The sulfite is filtered, dried, and calcined to release SO_2 and to form magnesium oxide. The oxide is slaked with water to form magnesium hydroxide slurry which is used for the absorption of SO_2.

State of development Mitsui Miike Machinery Co. has operated a pilot plant designed to treat 1,500scfm flue gas. Recently it has been decided to build a commercial plant with a capacity of treating 294,000scfm of tail gas from a Claus furnace at Chiba refinery, Idemitsu Kosan. The plant will cost about $6.8 million and will be completed by February 1974.

7.7 MHI-IFP ammonia process[7)]

Developer Mitsubishi Heavy Industries
5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Process description This process is a combination of ammonia scrubbing with thermal decomposition and the IFP process to produce sulfur from SO_2 and H_2S (Figure 7.7). A hot waste gas containing SO_2 is first introduced into a cooling section at a lower part of a reactor, where the gas is contacted with an ammonium sulfite solution. The gas is cooled and a portion of SO_2 is absorbed to form bisulfite while the solution is concentrated. The gas is then led into an absorbing section, where most of the SO_2 is absorbed by an ammonium sulfite solution. The bisulfite solution is discharged from the absorbing section and neutralized with ammonia coming from an ammonia recovery section and an IFP reactor to form an ammonium sulfite solution. Most of the sulfite solution is recycled to the absorbing section and a portion is sent to the cooling section. The gas is then passed through an ammonia recovery section, reheated and emitted.

The liquor discharged from the cooling section of the reactor contains ammonium sulfite, bisulfite, sulfate (formed by oxidation of the sulfite), and some thiosulfate (formed by a small amount of H_2S in ammonia from the IFP reactor). The liquor is led into a first-stage evaporator where ammonium sulfite and bisulfite are decomposed to form ammonia, SO_2 and water vapor. Ammonium sulfate and thiosulfate are decomposed in a sulfate reduction reactor by the reaction with H_2S on heating to form ammonia, SO_2 and water vapor.

$$(NH_4)_2SO_3 = 2NH_3 + H_2O + SO_2$$

$$NH_4HSO_3 = NH_3 + H_2O + SO_2$$

$$(NH_4)_2S_2O_3 = 2NH_3 + H_2S + SO_2 + H_2O$$

$$3(NH_4)_2SO_4 + H_2S = 4SO_2 + 6NH_3 + 4H_2O$$

$$3NH_4HSO_4 + H_2S = 3NH_3 + 4H_2O + 4SO_2$$

The gases formed by the decomposition are sent to an IFP reactor along with H_2S to produce molten sulfur.

$$2H_2S + SO_2 = 3S + 2H_2O$$

The gas leaving the IFP reactor contains ammonia, water vapor, and small amounts of SO_2 and H_2S, and is led into the absorber along with the waste gas containing SO_2.

State of development The ammonia scrubbing and the decomposition steps have been developed by Mitsubishi Heavy Industries since 1962. The IFP process has been developed by I.F.P., France. A commercial plant with a capacity of treating 16,000scfm of tail gas from a Claus furnace is under construction at Shimozu (Wakayama) plant, Maruzen Oil Co. to start operation in 1974.

Advantages Elemental sulfur is obtained as a by-product. No wastewater. SO_2 in waste gas and H_2S in tail gas can be recovered simultaneously.

Disadvantages The process is not simple. Not easy to apply to plants which have no H_2S.

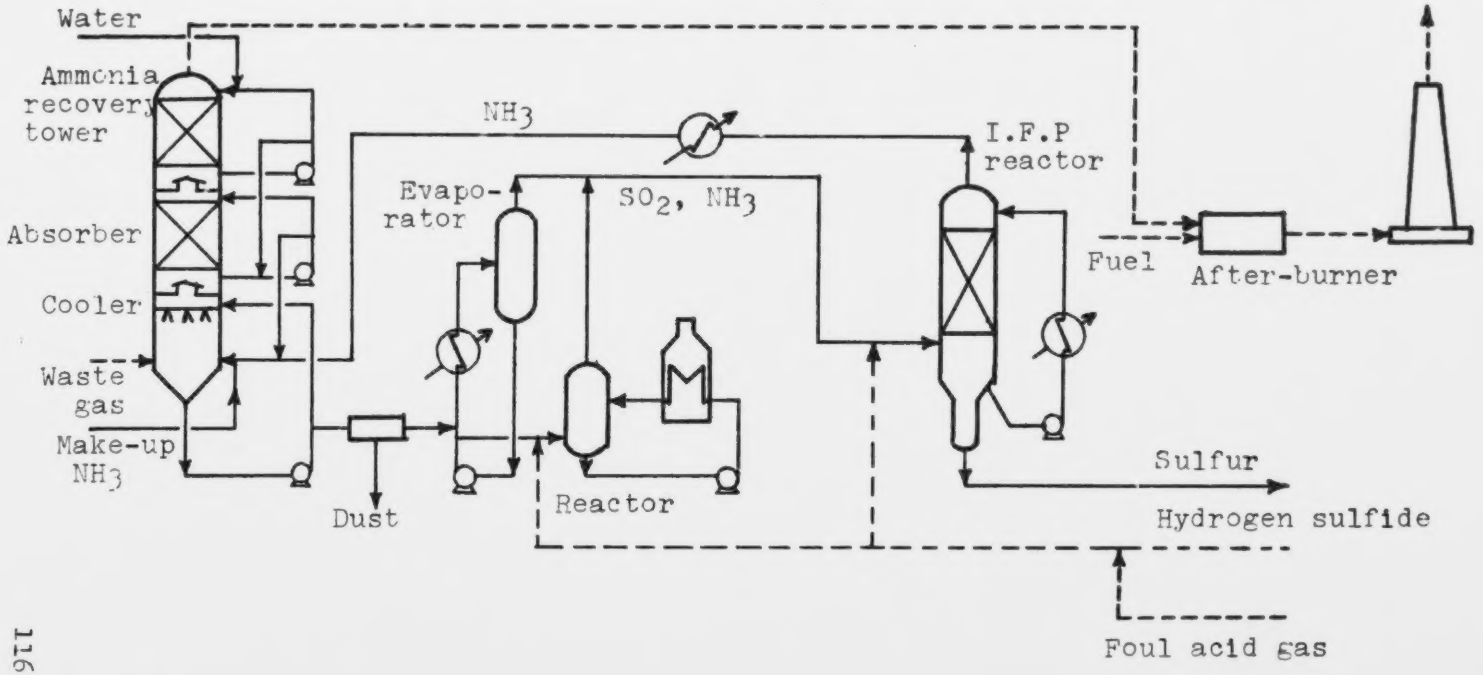

Water
Ammonia recovery tower
Absorber
Cooler
Waste gas
Make-up NH_3
Dust
NH_3
Evaporator
SO_2, NH_3
Reactor
I.F.P reactor
Fuel
After-burner
Sulfur
Hydrogen sulfide
Foul acid gas

Figure 7.7 Flow sheet of M.H.I.- I.F.P. process

7.8 Hitachi Shipbuilding sodium hypochlorite process

Developer Hitachi Shipbuilding & Engineering Co.
1-47, Edobori, Nishi-ku, Osaka

Process description Waste gas is treated by a scrubber with a pH 8.5-10 solution of NaClO (about 2 lb/gal) containing some calcium hydroxide. About 95% of SO_2 is removed to precipitate gypsum which is then filtered off.

$$NaClO + H_2O + SO_2 = H_2SO_4 + NaCl$$

$$H_2SO_4 + Ca(OH)_2 = CaSO_4 \cdot 2H_2O$$

The filtrate contains NaCl and small amounts of sulfuric acid and impurities. Calcium hydroxide is added to the filtrate to precipitate the impurities with some gypsum, which are then filtered off. The filtrate is subjected to electrolysis to regenerate the absorbing solution which contains NaClO and $Ca(OH)_2$.

State of development A pilot plant with a capacity of treating 300scfm of flue gas has been in operation.

Advantage High recovery of SO_2 is attained and gypsum is by-produced without scaling problems.

Disadvantage The process includes electrolysis and might be fairly costly.

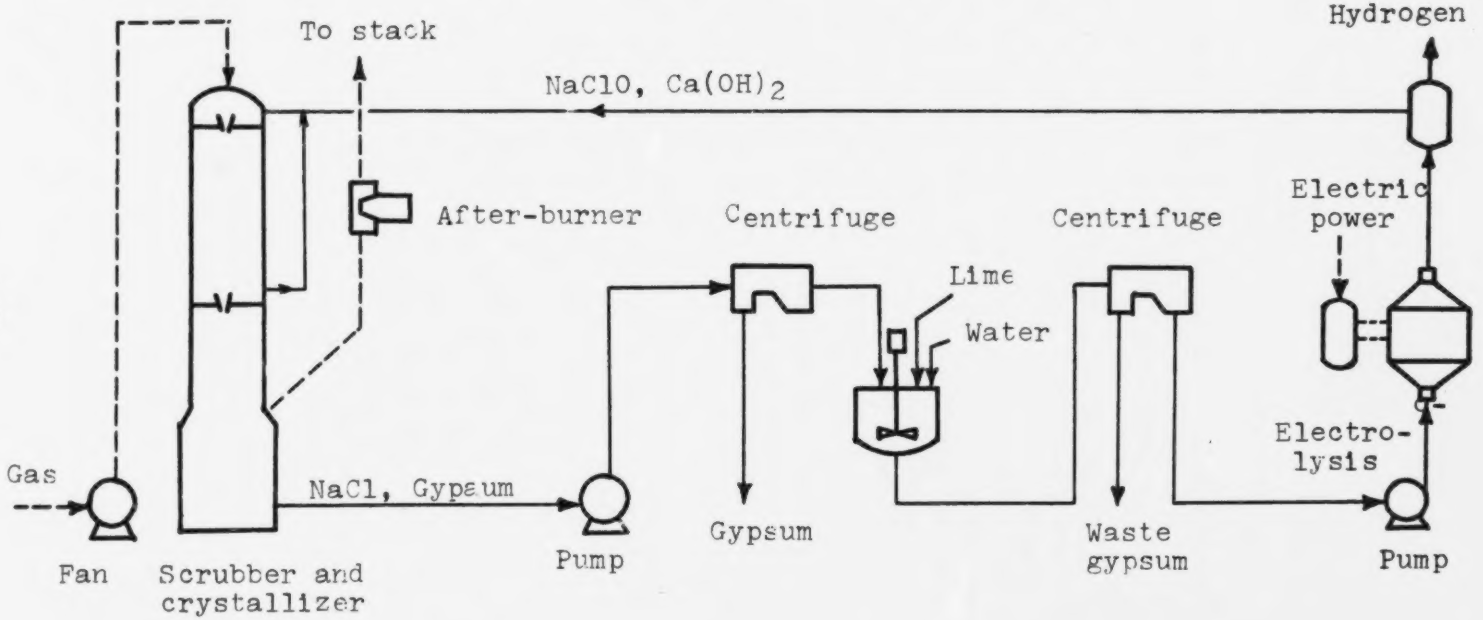

To stack
Hydrogen
NaClO, Ca(OH)$_2$
After-burner
Centrifuge
Centrifuge
Electric
power
Lime
Water
Electro-
lysis
Gas
NaCl, Gypsum
Fan
Scrubber and
crystallizer
Pump
Gypsum
Waste
gypsum
Pump

Figure 7.8 Flow sheet of Hitachi Shipbuilding sodium hypochlorite process (HD process)

8 Dry process

8.1 Hitachi activated carbon process[7, 8)

Developer Hitachi Ltd.
2-8, Otemachi, Chiyoda-ku, Tokyo

Process description Flue gas from oil-fired boiler (247,000scfm) at 280°F after passing through an electrostatic precipitator is led into adsorbers with fixed beds of activated carbon (particle size about 1/4 in.)

The adsorption system consists of two parallel trains of three towers in series (Figure 8.1). Each tower has three fixed beds and operates at a gas velocity of about 1.5 ft/sec. The vessels are of mild steel coated with a phenolic resin. The operation of each tower is **cyclic** with adsorption, washing, and drying occurring sequentially in each bed. During the wash stage, gas flow is diverted by louvered dampers to another bed. The total cycle time is 63 hours; 7 hours wash and the rest for drying and adsorption. The adsorbed SO_2 oxidizes in place to SO_3 and is collected as 20% H_2SO_4 by water washing. Removal efficiency of SO_2 in the gas is above 80%. The acid is reacted with pulverized limestone to produce salable gypsum. Batch centrifuges are used to separate the product. After the gypsum is removed, the liquor is discharged to the wastewater treatment system. Soot in the liquor would plug the carbon pores if the effluent were recycled for washing the beds.

State of development The 247,000scfm plant has been in operation at Kashima station, Tokyo Electric Power since 1972.

Prior to the construction, a pilot plant (90,000scfm) was operated at Goi station, Tokyo Electric Power. During the operation of the pilot plant, tests were made to concentrate the weak acid to 65% by submerged combustion. However, operating problems and economics indicated that production of gypsum would be a better approach for the larger plant at Kashima. At Kashima, attempts have been made to eliminate the wastewater from the gypsum production step. For example, the weak sulfuric acid is concentrated to 50 to 70% by contacting with flue gas and then reacted with pulverized limestone. Excessive water is volatilized by the heat of the reaction. Dry gypsum, suitable as a retarder of cement setting, is obtained. A small pilot plant based on this process has been in operation.

Economics The 247,000scfm plant cost $5.8 million including 550 tons of activated carbon which costs $87/ton. About 20% of the carbon is consumed in a year. The desulfurization cost including depreciation (in 7 years) and revenue from by-produced gypsum ($6/ton) is estimated to be $1.1/bl oil or 1.7 mil/kWh.

Advantages The process is simple. Operation is safe and easy. The gas temperature is maintained above 210°F so that no reheating is required. Good quality gypsum is obtained.

Disadvantages Investment and desulfurization costs are higher than those by wet processes. A considerable amount of wastewater is emitted although it is neutral and does not contain much impurity. The new step for gypsum production can eliminate wastewater but requires the concentration of sulfuric acid.

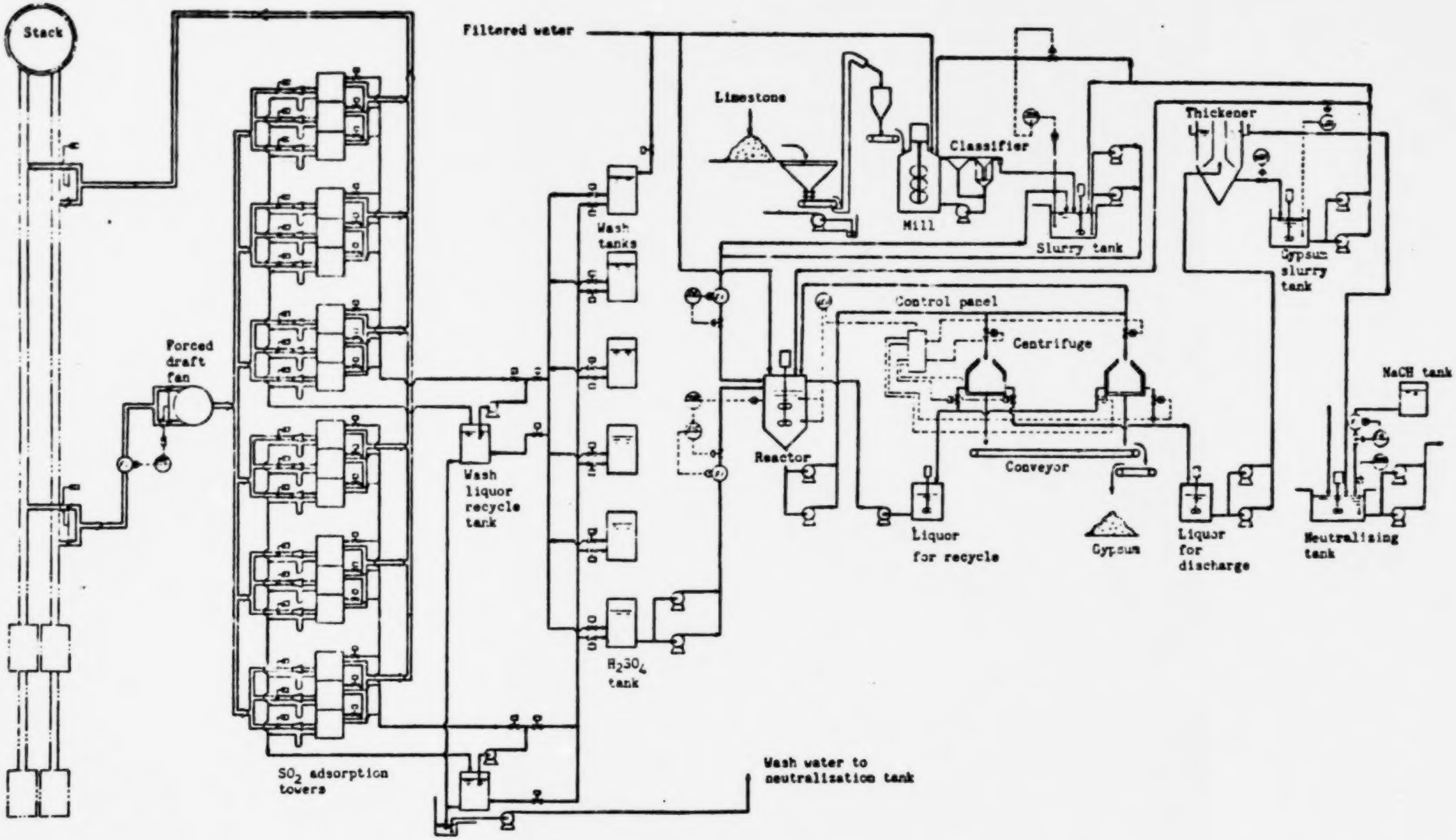

Stack
Forced draft fan
SO$_2$ adsorption towers
Wash liquor recycle tank
Filtered water
Wash tanks
H$_2$SO$_4$ tank
Wash water to neutralization tank
Limestone
Mill
Classifier
Slurry tank
Thickener
Gypsum slurry tank
Control panel
Centrifuge
Reactor
Conveyor
Liquor for recycle
Gypsum
Liquor for discharge
NaCH tank
Neutralizing tank

Figure 8.1.1 Hitachi activated carbon process

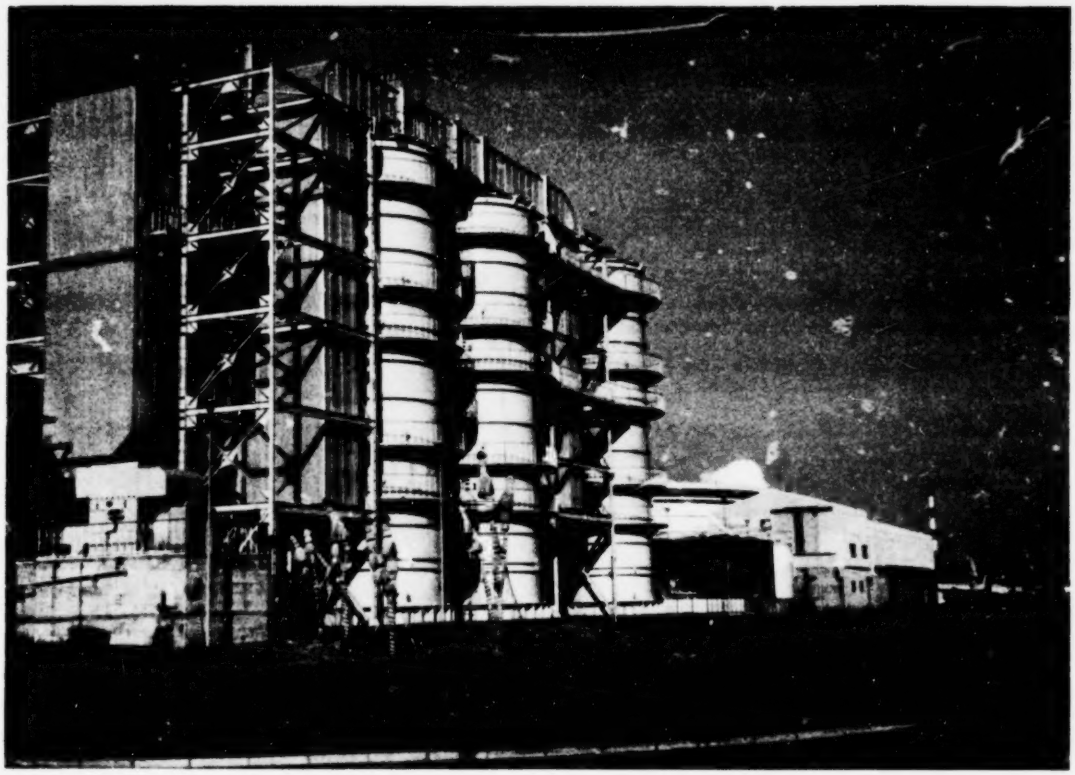


Figure 8.1.2 Kashima plant, Tokyo Electric Power
(Hitachi activated carbon process)

8.2 Sumitomo activated carbon process[7, 8]

Developer Sumitomo Shipbuilding and Machinery Co. Ltd.
2-1, 2-chome, Otemachi, Chiyoda-ku, Tokyo

Process description Moving beds of activated carbon are used for SO_2 recovery. A flow sheet is shown in Figure 8.2. Flue gas from an oil-fired boiler at 285°F (100,000scfm) is first led into a mechanical collecter for dust removal, then cooled to 250°F by water spray. The gas is split between two parallel vessels containing moving beds of granular activated carbon. The system is designed to recover 80% of the SO_2 when oil containing 2% sulfur is burned. The carbon is introduced at the top of the adsorber and moved downward, while the gas flows across the bed. The loaded carbon is transferred by an inclined conveyor to the top of a single desorption tower where the moving bed is contacted with hot inert gas at 600 to 700°F in a cross flow configuration to release SO_2. The inert gas is produced by controlled combustion of butane, The SO_2 concentration in the desorber exhaust gas is controlled to a range of 10 to 20%. A large portion of the gas is returned to the desorber through a heat exchanger and the rest is sent to a sulfuric acid plant of a conventional contact process. Tail gas from the sulfuric acid plant is returned to the SO_2 absorption system. The carbon after the desorption is cooled to 220°F at the lower part of the desorber, screened to remove fines, and returned to the absorber.

State of development A pilot plant treating 6,000scfm flue gas was put in operation in 1967. A prototype plant with a capacity of treating 100,000scfm was completed by the end of 1971 at Sakai Plant, Kansai Electric Power and put in operation in February 1972. The plant has been under nearly continuous operation except for a few months' boiler outage.

Sumitomo has also developed a wet-desorption process in which the loaded carbon on a horizontally moving bed is continuously washed with water to produce dilute sulfuric acid of 10 to 20% concentration. A pilot plant with a capacity of treating 6,000scfm has been in operation with this system.

Status of technology The carbon bed of the prototype plant moves very slowly requiring two days for one cycle. Nearly 1% of the carbon is consumed in one cycle mainly by mechanical degradation forming powder and partly by chemical reaction. Tests have been made to improve the quality of the carbon and also to reuse the powdered carbon by granulation. The ratio of the inert gas for the desorption to the flue gas is maintained at 200.

Economics The prototype plant cost $2.8 million including the sulfuric acid plant with a capacity of producing 20 tons of sulfuric acid (98% concentration) per day. The carbon costs $90/ton.

Advantages The gas temperature is reduced only slightly, so that no reheating is required. The process is simple and operation is safe and easy. The continuous cross flow of gas and carbon ensures stable adsorption and desorption. Very little wastewater is emitted. Concentrated sulfuric acid is obtained by the dry desorption process.

Disadvantages Investment cost is relatively high. The desulfurization cost seems to be relatively high as well unless cheaper activated carbon is available. By the wet-adsorption process, the carbon consumption is less but the product acid is weak.

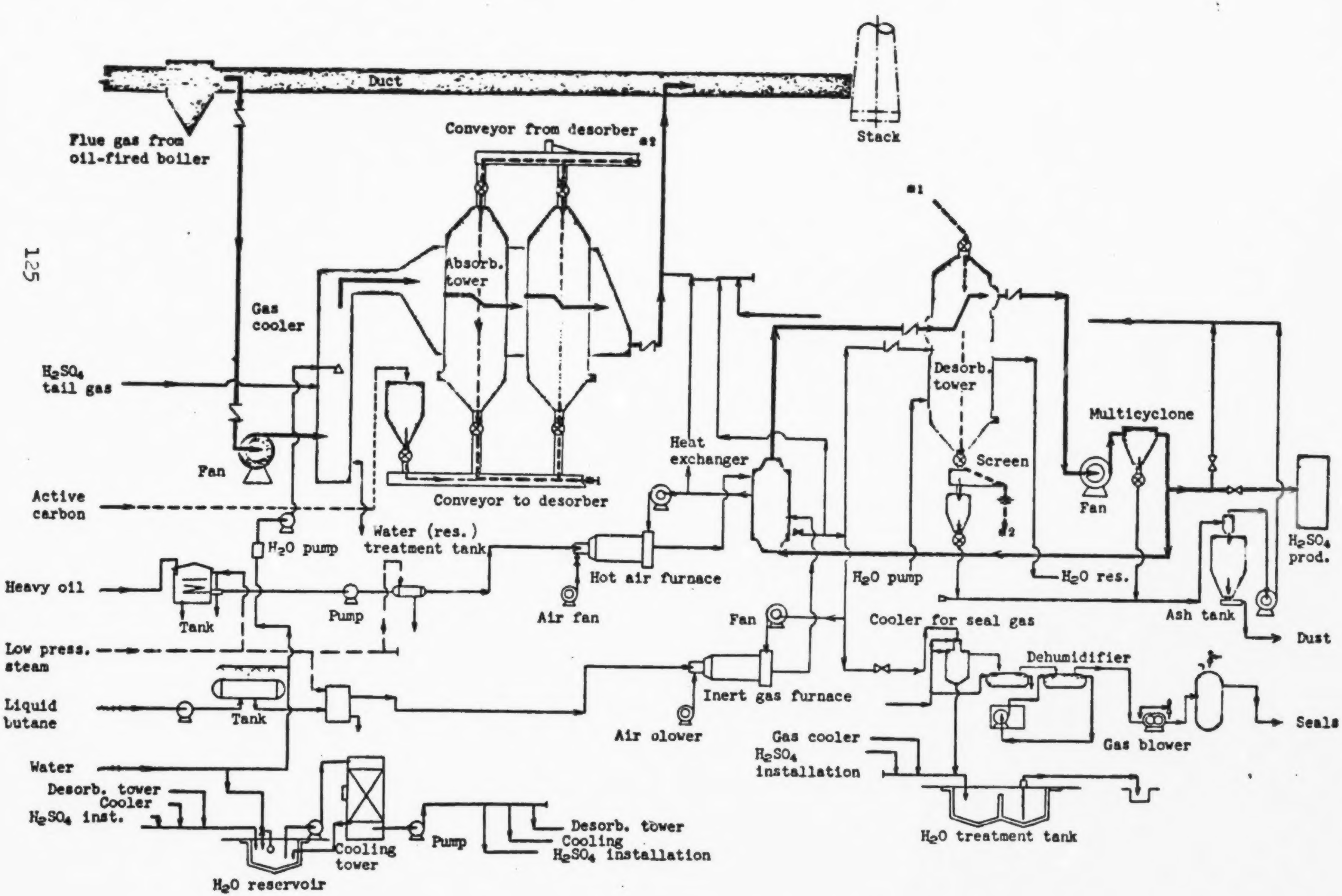

Duct
Stack
Flue gas from oil-fired boiler
Conveyor from desorber
a2
a1
Absorb. tower
Gas cooler
H_2SO_4 tail gas
Fan
Active carbon
Conveyor to desorber
H_2O pump
Water (res.) treatment tank
Heavy oil
Tank
Pump
Low press. steam
Liquid butane
Tank
Water
Desorb. tower Cooler H_2SO_4 inst.
H_2O reservoir
Cooling tower
Pump
Desorb. tower
Cooling
H_2SO_4 installation
Heat exchanger
Hot air furnace
Air fan
Fan
Inert gas furnace
Air blower
Desorb. tower
Screen
a2
Multicyclone
Fan
H_2O pump
H_2O res.
H_2SO_4 prod.
Ash tank
Dust
Cooler for seal gas
Dehumidifier
Gas blower
Seals
Gas cooler
H_2SO_4 installation
H_2O treatment tank

Figure 8.2.1 Sumitomo activated carbon process

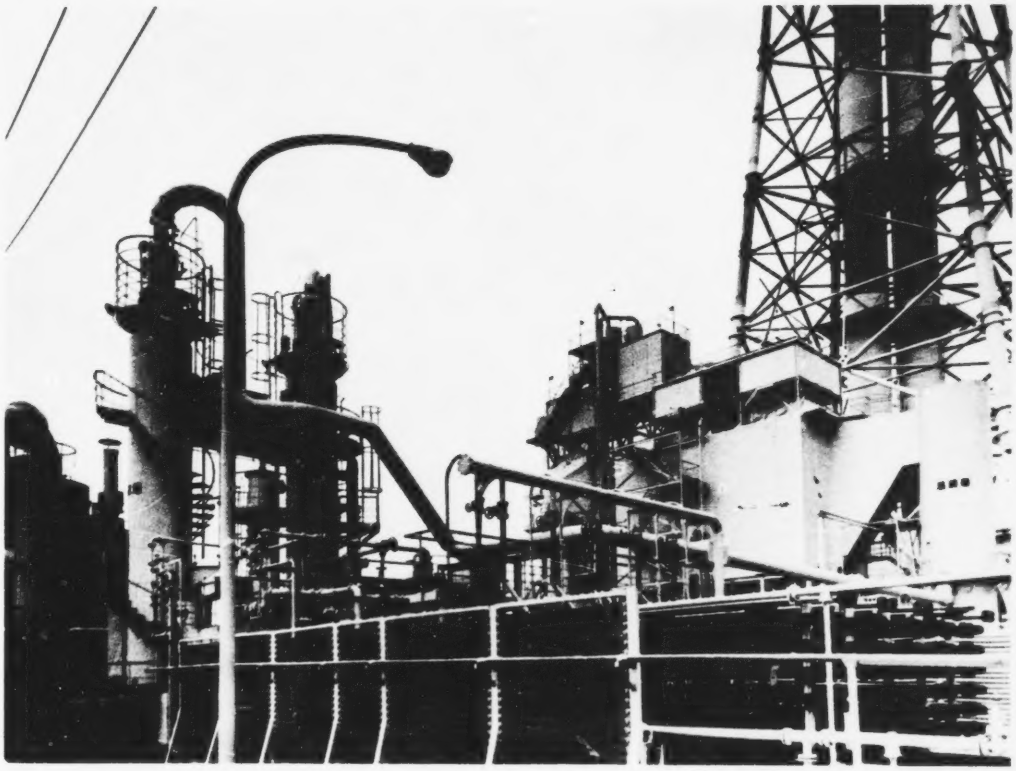


Figure 8.2.2 Sakai plant, Kansai Electric Power

(Sumitomo activated carbon process)

8.3 Mitsubishi manganese process (DAP-Mn process)7)

Developer Mitsubishi Heavy Industries
5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Process description Activated manganese oxide $MnO_x \cdot nH_2O$ in powder form (5 to 150 microns in size) is charged into an absorber, and is dispersed and carried by flue gas. The powder is caught by a multiclone and electrostatic precipitator with an efficiency of 99.99%. About 90% of SO_2 in the gas is removed, forming magnesium sulfate. The powder caught is a mixture of the oxide and sulfate with some dust from the boiler. Most of the powder is returned to the absorber. The rest is treated with water to dissolve the sulfate; the unreacted oxide which is insoluble in water is centrifuged and returned to the absorber; the dust is removed during this step. The manganese sulfate solution is treated with ammonia and air to precipitate activated manganese oxide. The mother liquor is concentrated to obtain solid ammonium sulfate which has more than 99% purity.

State of development A prototype plant to treat $150{,}000 Nm^3/hr$ flue gas from an oil-fired boiler was completed at Yokkaichi, Chubu Electric Power in 1967 under contract with the Agency of Industrial Science and Technology. A semicommercial plant to treat 193,000scfm gas (110MW equivalent) has been in operation since February 1972 at Yokkaichi.

Operation of semicommercial plant The plant deals with half of the flue gas from a 220MW oil-fired boiler; the rest of the gas is emitted without being desulfurized. Therefore, oil with a relatively low sulfur content has been burned giving a flue-gas SO_2 concentration of about 900ppm. The temperature of the inlet gas is 275°F and that of outlet gas 230°F. The outlet gas contains 90ppm SO_2 (90% recovery) and less than 0.005grain/scf dust. The pressure drop by the absorber is only 0.4 in.H_2O; that of the whole system including the dust eliminators is 6 in.H_2O. The operation has been carried out satisfactorily except for an erosion problem of the centrifuge for separating the unreacted manganese oxide. The power station is shut down several times a month, and moreover, the operation load varies frequently due to changes in power demand. The desulfurization plant is well automated for ease of shutdown, restart, as well as for the control of operation load. However, when the amount of inlet gas decreases to below half of the normal volume, dispersion of the manganese oxide as well as the dust removal efficiency of the multiclone become unsatisfactory.

Economics The investment cost for the semicommercial plant (110MW) is \$4.5 million. The desulfurization cost would be a little more than \$1/bl oil.

Advantages The absorbent, which is highly reactive and in powder form, enables SO_2 to be recovered at a high rate. Pressure drop through the absorber is very low. Temperature drop in the gas is also small. The gas temperature after desulfurization is kept at 230°F.

Disadvantages The desulfurization cost is relatively high. Demand for ammonium sulfate is decreasing.

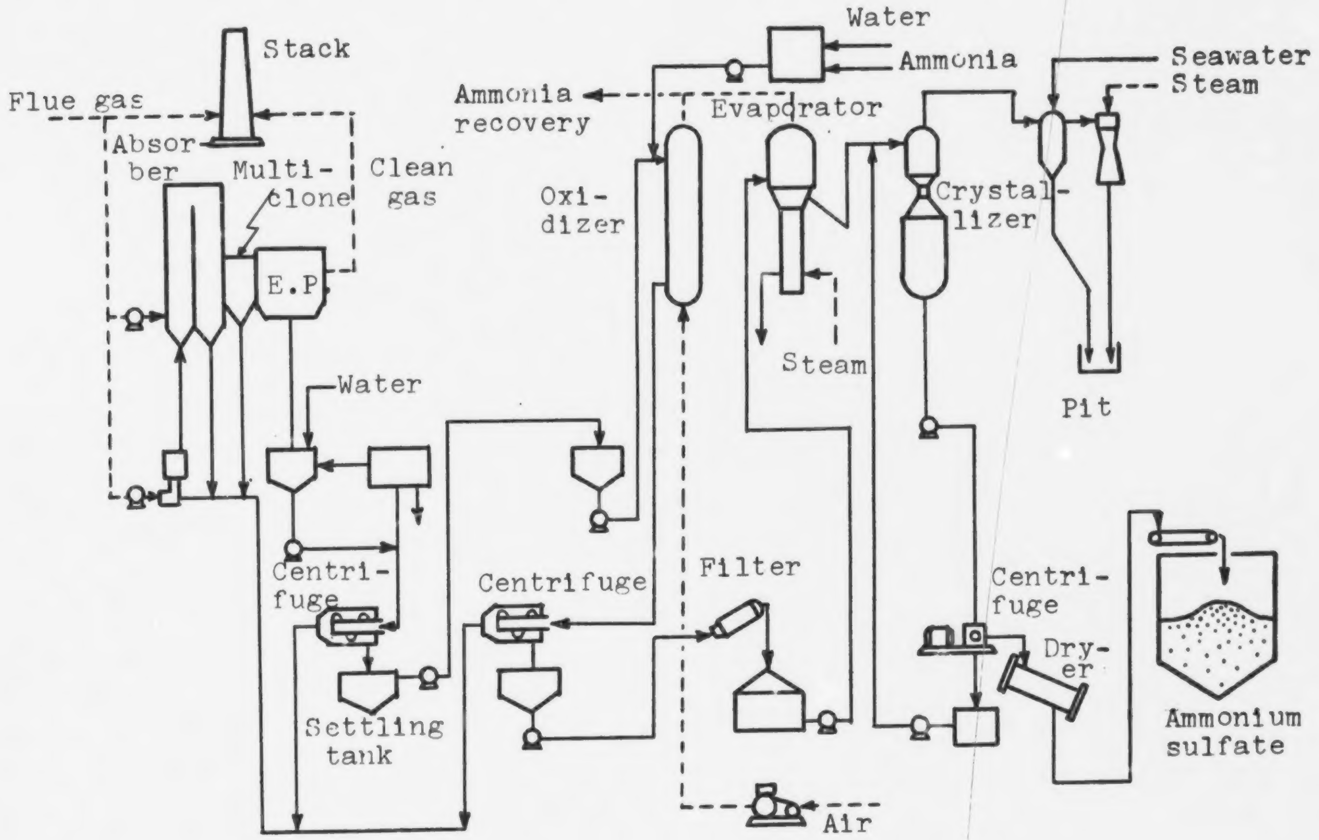

Stack
Flue gas
Absorber
Multiclone
Clean gas
E.P
Water
Centrifuge
Settling tank
Ammonia recovery
Oxidizer
Centrifuge
Water
Ammonia
Evaporator
Steam
Filter
Air
Crystallizer
Seawater
Steam
Pit
Centrifuge
Dryer
Ammonium sulfate

Figure 8.3.1 Flow sheet of Mitsubishi DAP-Mn process

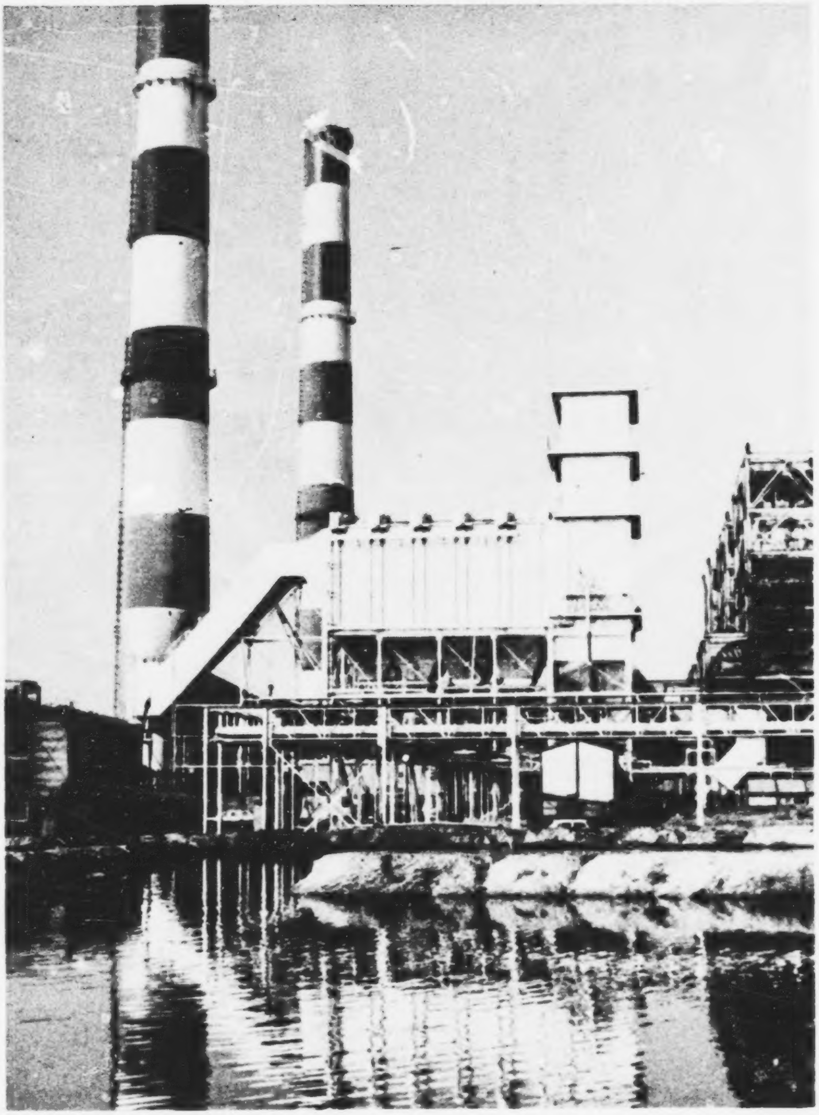


Figure 8.3.2 Yokkaichi plant, Chubu Electric Power Co. (193,000scfm, Mitsubishi manganese process)

8.4 Shell cupric oxide process[12)]

Developer Shell Group, Netherland

Licensor in the Far East Japan Shell Technology Co.
2-5, 3-chome, Kasumigaseki, Chiyoda-ku, Tokyo

Process description SO_2 in flue gas at 750°F is absorbed by a cupric oxide catalyst held by an aluminum carrier. The cupric sulfate thus formed is then reduced with a reducing gas rich in hydrogen to release SO_2 and regenerate the cupric oxide.

$$Cu + 1/2O_2 = CuO$$

$$CuO + SO_2 + 1/2O_2 = CuSO_4$$

$$CuSO_4 + 2H_2 = Cu + SO_2 + 2H_2O$$

Two towers packed with the cupric oxide absorbent are provided, the two alternating between absorption and regeneration every hour. The life of the absorbent is estimated to be about 8,000 cycles. The SO_2 gas recovered will be led into a Claus furnace to react with hydrogen sulfide gas to produce elemental sulfur. In plants which have no source of hydrogen sulfide, a portion of the SO_2 gas is reduced to form hydrogen sulfide.

State of development A plant with a capacity to treat 70,600scfm flue gas from an oil-fired boiler is under construction at Yokkaichi Refinery, Showa Yokkaichi Sekiyu Co. to start operation in August 1973. This plant will be the world's first commercial plant to use the Shell process; Shell has made pilot plant tests in the Netherlands to treat 590scfm gas.

Advantages The temperature of the outlet gas is high, so that no reheating is required. Elemental sulfur is obtained as a by-product.

Disadvantage Application is not easy for plants which have neither reducing gas nor hydrogen sulfide.

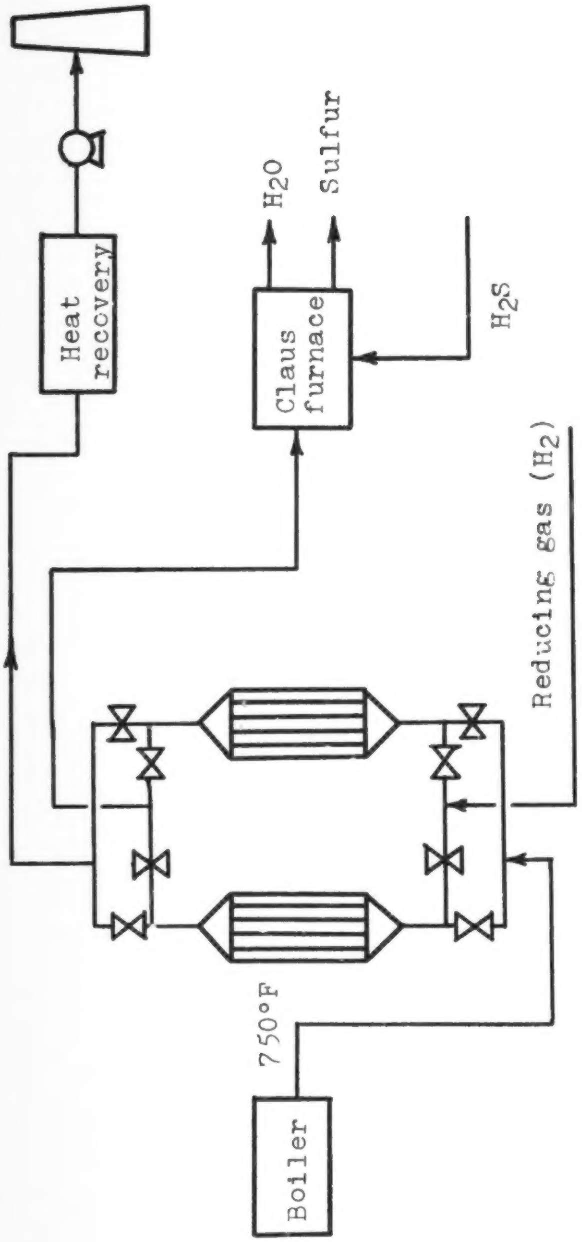

Boiler
750°F
Reducing gas (H_2)
Claus furnace
H_2S
H_2O
Sulfur
Heat recovery

Figure 8.4 Flow sheet of Shell cupric oxide process

8.5 Other dry processes

8.5.1 Hitachi Shipbuilding reduction process

Hitachi Shipbuilding & Engineering Co. (1-47, Edobori, Nishi-ku, Osaka) made bench scale tests of a reduction process originally developed by Chevron Chemical, U.S.A. to reduce SO_2 and NO_x to sulfur and nitrogen simultaneously by reacting with carbon monoxide in the presence of a catalyst. As the catalyst was readily damaged by oxygen and water vapor present in small **amounts** in the gas, improvements have been made by Hitachi on the process as well as on the catalyst. By the improved process, vanadium and nickel in flue gas which are poisonous **to** the catalyst are first removed, then most of SO_2 is absorbed by an iron-manganese oxide forming sulfates. The gas is then reacted with carbon to form carbon monoxide. The gas containing carbon monoxide is again reacted with the iron-manganese oxide for further desulfurization and is finally subjected to NO_x removal by reduction in the presence of a catalyst. The sulfates are decomposed by heating to release SO_2 and to regenerate iron-magnesium oxide. A pilot plant (5,900scfm) is under construction at Sakai refinery, Kansai Oil to start operation in May 1973.

8.5.2 NRIPR active sodium carbonate process

National Research Institute of Pollution and Resources (188, Kotobukicho, Kawaguchi-shi, Saitama Prefecture) has operated a pilot plant (100scfm) to absorb SO_2 with sodium carbonate powder, as was described in the 1972 report. Sodium sulfate formed by the reaction is reduced by a reducing gas (H_2 and CO) to produce H_2S and to regenerate sodium carbonate. There has not been much progress during the past year or so, except for some improvement in the reduction process. The reduction process is not simple and seems fairly costly.

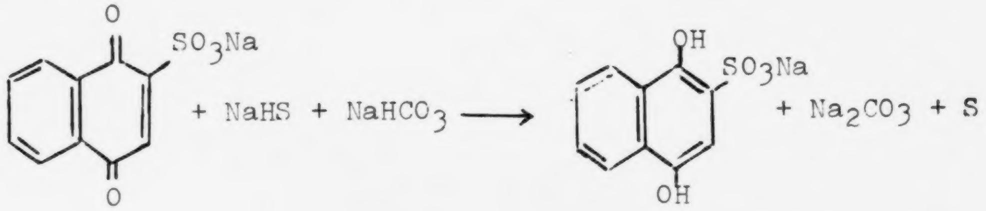
9 New processes for H_2S recovery

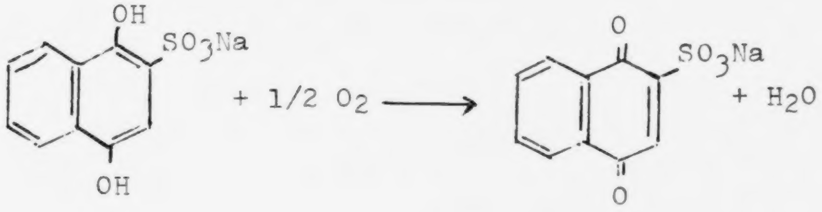
9.1 Takahax process

Developer Kinon Chemicals
3-3, 1-chome, Ginza Nishi, Chuo-ku, Tokyo

Process description Hydrogen sulfide is recovered by an alkaline solution at pH 8 to 8.5 containing a newly developed catalyst 1,4-naphthoquinone-2-sulfonic acid, which precipitates elemental sulfur rapidly. The catalyst is readily regenerated by introducing air into the solution.

$$H_2S + Na_2CO_3 = NaHS + NaHCO_3$$





More than 99.8% of hydrogen sulfide in coke oven gas, petroleum gas, etc. is recovered. 1,4-naphthoquinone is recovered easily from the sludge by-produced when phthalic anhydride is produced from naphthalene. It can also be directly synthesized at a high yield. It can be easily converted to 1,4-naphthoquinone-2-sulfonic acid, which is soluble in water. Two towers--absorber and oxidizing tower--are used for the cleaning of fuel gas, etc. (Figure 9.1, A). For the desulfurization of waste gas, one tower is used into which both air and the gas containing hydrogen sulfide are introduced (Figure 9.1, B). The recovery of hydrogen sulfide is not hindered by the impurities in the gas such as hydrogen cyanide and oil mist. If required, hydrogen cyanide can also be removed in the form of a rhodanate.

The following values have been adopted recently as operating conditions.

Alkali concentration	About 4% as Na_2CO_3
pH	8 to 8.5
Catalyst concentration	0.05 - 0.07 moles/gallon
Make-up chemicals	Catalyst: 0.01 mole/lb of recovered sulfur Alkali: 0.15 lb/lb of recovered sulfur
Power requirement	1.4kWh/1,000scf gas

State of development The process has been adopted recently in about 100 plants in Japan. Some of the plants are shown below.

User	Plant site	Capacity (1,000scfm)	Source of gas	Year of completion
Sumitomo Metal	Wakayama	47	Coke oven	1971
Kawasaki Steel	Chiba	15	Coke oven	1971
Yamato Boseki		26	Rayon plant	1972
Kuraray Co.		59	Rayon plant	1972
Futamura Chem.		6	Cellophane plant	1972
Toyobo		35	Rayon plant	1973
Nippon Steel	Yokkaichi	147	Coke oven	1973
Nippon Steel	Yokkaichi	147	Coke oven	1974

The process has undergone improvement recently. The improved process (New Takahax process) will be used for Nippon Steel's Yokkaichi plant, where two units are being built to treat 147,000scfm of coke oven gas each.

Possible application The Takahax process has so far been utilized chiefly in the town gas industry and iron industry, especially for the desulfurization of coke oven gas. Since the catalyst is highly stable and active, the process is thought to be applicable to various gases regardless of the concentration of hydrogen sulfide, for example for the recovery of hydrogen sulfide from hydrodesulfurization of heavy oil as well as the sulfide in the tail gas of a Claus furnace. Also in treating waste fermentation gas, the process is utilized to give methane gas which may be used as a heat source for boilers.

The new Takahax process may be helpful in removing heavy metals in wastewater by using hydrogen sulfide which is quite effective in precipitating heavy metals but has not been used for that purpose because of the difficulty in treating the gas released to the air.

Economics The Takahax process and the Thylox process are compared below with regard to investment and operation costs. The investment cost for treating 5,900scfm for 2.2 grains/scf H_2S by the Takahax process is as follows:

Remote-control system	$230,000
Field operation system	$204,000

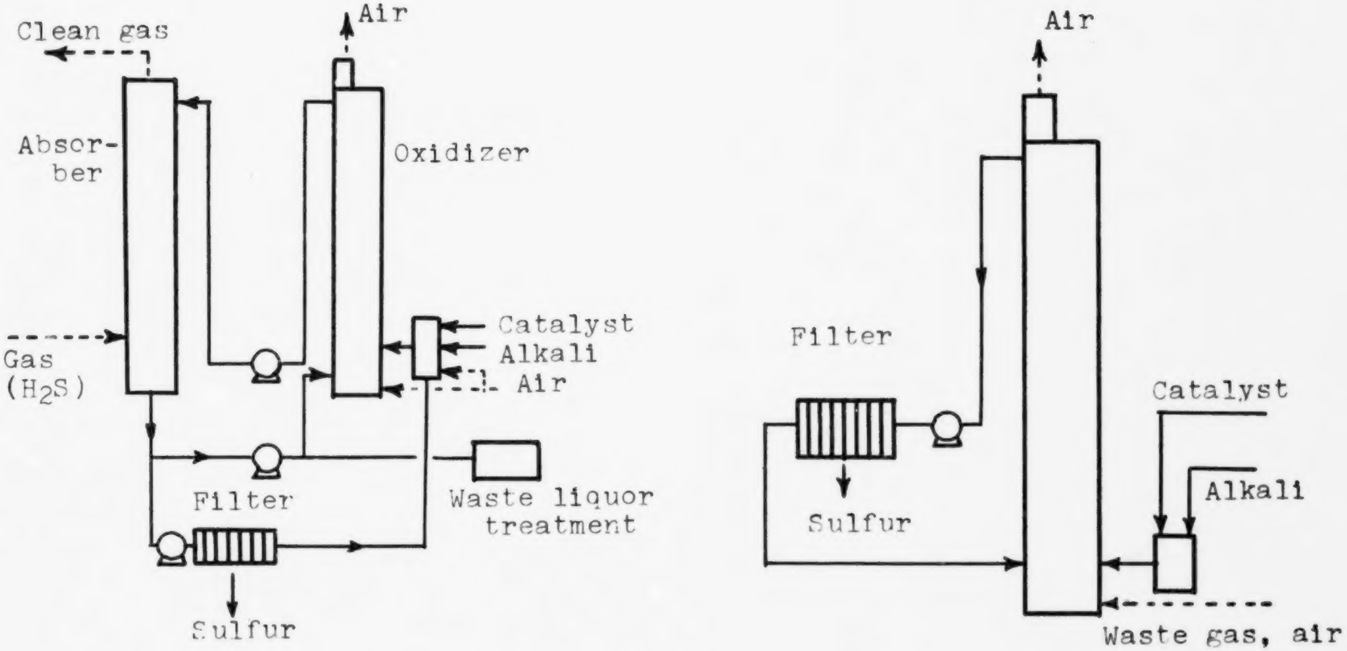
On the other hand, the Thylox process costs $306,000, or about 40% more. The cost per 1,000scf of raw gas calculated from fixed and variable costs is:

Takahax process	about 2.1¢
Thylox process	about 4.2¢

The Thylox process requires an additional expenditure of 2.0¢ or so for arsenic removal.

Advantages Both investment and operation costs are low. Very high recovery of H_2S--more than 99.8%--is attained. Operation is so easy that unattended operation is possible. The catalyst is not poisonous, so that the by-product sulfur is useful.

Disadvantage The filtered sulfur is powdery and contains some alkali; washing is required for utilization.


Clean gas
Air
Absorber
Oxidizer
Catalyst
Alkali
Air
Gas (H_2S)
Filter
Waste liquor treatment
Sulfur
Air
Filter
Catalyst
Alkali
Sulfur
Waste gas, air

(A) Two-tower system

(B) One-tower system

Figure 9.1.1 Flow sheet of Takahax process

9.2 Fumaks and Rhodacs processes

Developer Osaka Gas Co. Ltd.

Sumitomo Chemical Engineering Co.
3-33, Hongo, Bunkyo-ku, Tokyo

Process description Gas containing H_2S is washed in a spray tower with the Fumaks solution--an alkaline solution containing 0.1% catalyst (picric acid) in 2-3% aqueous solution of sodium carbonate or in dilute aqueous ammonia (Fumaks process). More than 99% of the H_2S is absorbed by the following reaction:

$$NH_4OH + H_2S = NH_4HS + H_2O$$

The liquid that has absorbed H_2S is sent to a regeneration tower, where the liquid is sprayed to contact air and to undergo the following oxidation reaction:

$$NH_4HS + 1/2O_2 \xrightarrow{\text{picric acid}} NH_4OH + S$$

Sulfur is precipitated, then filtered off. The regenerated aqueous ammonia containing picric acid is recycled to the absorption step. The by-produced sulfur contains about 48% water after the filtration. More than 99% sulfur is contained on a dry basis. The sulfur can be used for sulfuric acid production.

When the gas contains both H_2S and HCN as in the case of coke oven gas, those can be removed by the following reaction (Rhodacs process):

$$2NH_3 + H_2S + xS = (NH_4)_2S_{x+1}$$

$$(NH_4)_2S_{x+1} + HCN + NH_3 = NH_4SCN + (NH_4)_2S_x$$

The sulfur required for the reaction can be produced by the Fumaks process. Thus by the combination process of Fumaks and Rhodacs, H_2S and HCN in the gas can be removed simultaneously. The following chemicals are consumed by the combination process:

Picric acid	30 lb/ton H_2S
Ammonia	0.3 lb/ton H_2S and 1.2 lb/ton HCN

State of development Nineteen commercial plants using the Fumaks process and two commercial plants using the combination process have been built in various parts of Japan. Some of them are shown in the following table.

Process	User	Plant site	Amount of gas treated (scfm)	Completed
Fumaks	Osaka Gas	Sakai	21,200	1968
Fumaks	Osaka Gas	Nishijima	11,800	1970
Fumaks	Osaka Gas	Kobe	8,200*	1970
Combination	Amagasaki Coke	Ohama	34,700	1972
Combination	Sumikin Kako	Kashima	47,000	1972

* Oil gas; other figures are for coke oven gas.

Advantages The process is simple and operation is easy. High recovery of H_2S is attained by the Fumaks process using a cheap catalyst which is not poisonous. H_2S, HCN and NH_3 in coke oven gas can be removed simultaneously by the combination process.

Disadvantage The by-produced sulfur contains much moisture with some alkali and needs to be washed for utilization.

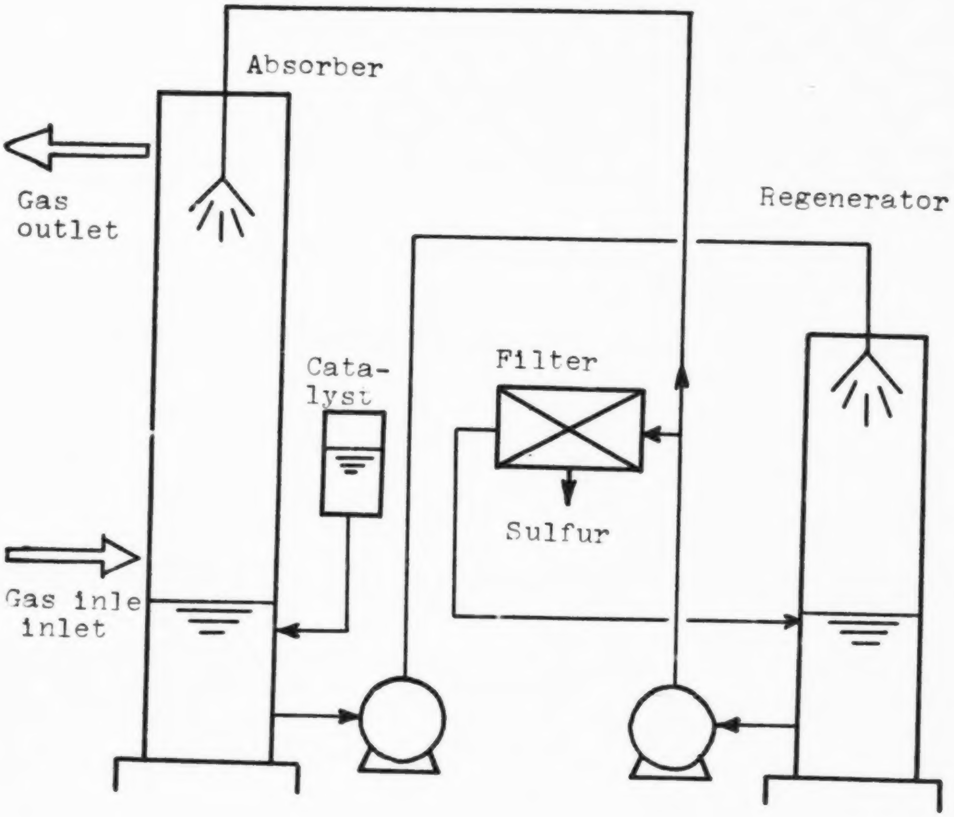

Absorber
Gas outlet
Regenerator
Cata-lyst
Filter
Sulfur
Gas inle inlet

Figure 9.2

Flow sheet of Fumaks (Rhodacs) process

9.3 IFP-MHI process7)

Developer IFP, France

Mitsubishi Heavy Industries
5-1, 2-chome, Marunouchi, Chiyoda-ku, Tokyo

Process description Tail gas from Claus furnace containing H_2S and SO_2 is treated by an IFP reactor to recover sulfur. The outlet gas from the reactor which usually contains 1,000-1,500ppm SO_2 and H_2S is led into an incinerator to burn H_2S to form SO_2, and then passed through a waste-heat boiler. Since further desulfurization is required today, the gas is then subjected to sodium scrubbing to reduce the SO_2 content of the outlet gas to below 100ppm. The sodium sulfite formed by the scrubbing is oxidized with air into sodium sulfate; the sulfate solution is discarded.

State of development The following plants have been built recently by Mitsubishi:

User	Plant site	Capacity (scfm)	Completed
Nippon Oil	Negishi	16,700	1971
Idemitsu Kosan	Hyogo	15,700	1972
Showa Oil	Kawasaki	3,300	1972
Kyokuto Oil	Chiba	10,900	1972

Advantages The IFP process is simple and operation is easy. Molten sulfur of high purity is obtained.

Disadvantage The content of SO_2 and H_2S of the outlet gas from the IFP reactor is fairly high so that additional sodium scrubbing is required in many districts.

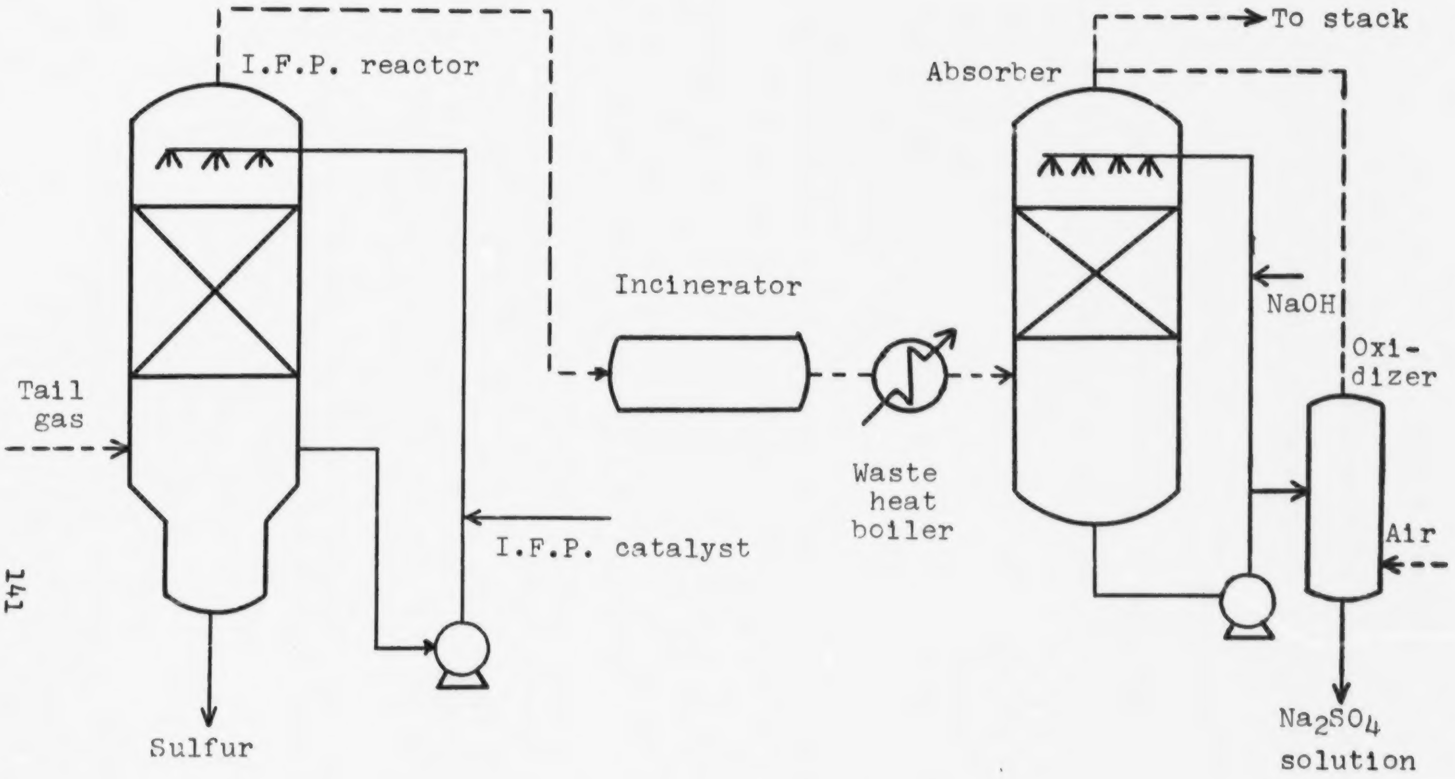

I.F.P. reactor
Tail gas
Sulfur
I.F.P. catalyst
Incinerator
Waste heat boiler
Absorber
To stack
NaOH
Oxi-dizer
Air
Na_2SO_4 solution

Figure 9.3 Flow sheet of IFP-MHI process

10 Economic aspects

10.1 Absorbents and by-products of desulfurization

The cost of absorbents for SO_2 is compared in Table 10.1.1.

Table 10.1.1 Costs of absorbents[14)]

Absorbent	Cost ($/t), (A)	Requirement per ton of SO_2* Amount (ton), (B)	Requirement per ton of SO_2* Cost ($), (A x B)
Caustic soda	67	1.25	83.8
Ammonia	67	0.53	35.5
Magnesium oxide	44	0.63	27.7
Slaked lime	17.5	1.16	20.3
Limestone	5.8	1.56	9.0
Activated carbon	940		

* Required to form sulfite or sulfate.

Limestone is the cheapest while activated carbon is most expensive. Since limestone is much cheaper than lime or slaked lime, there is a tendency to use pulverized limestone as in the processes of Mitsubishi-JECCO, Babcock-Hitachi, Kureha-Kawasaki, and Showa Denko.

For the production of waste sulfate or sulfite solution, either caustic soda, ammonia or magnesium oxide may be used. Although caustic soda is most expensive it has been used in most of the plants which produce waste products as shown in Table 4.4. This is because the scrubbing can be carried out most easily with sodium hydroxide, while ammonia tends to give plume problem and magnesium oxide is not as easy as sodium hydroxide solution to handle because it is insoluble in water.

The supply of sulfur and its compounds related to desulfurization is shown in Table 10.1.2. Their prices are shown in Table 10.1.3.

Table 10.1.2 Supply of sulfur and its compounds[4)]
(1,000 tons of material)

	1968	1969	1970	1971	1972
Sulfur					
Mined	283	180	120	47	18
Recovered	97	179	297	414	526
Total	380	354	417	461	544
Sulfuric acid					
from pyrite	4,576	4,524	4,303	3,348	2,747
from smelter gas	2,719	2,972	3,242	3,770	4,343
from sulfur	0	0	17	210	295
Total	7,295	7,496	7,562	7,328	7,385
Gypsum					
Mined	627	619	596	627	565
Phospho-gypsum	2,607	2,677	2,829	2,882	3,134
Other	277	288	577	656	704
Total	3,511	3,584	4,002	4,165	4,403
Sodium sulfite	268	307	398	420	435

Table 10.1.3 Price of sulfur and its compounds (\$/t)[4)]

	1967	1968	1969	1970	1971
Sulfur	73		54	68	50
Sulfuric acid	26	25	26	27	23
By-produced gypsum	4.4	4.7	4.4	6.1	6.7
Sodium sulfite(anhydrous)	64	62	61	58	60

The domestic supply of and demand for sulfur and its compounds have been fairly well balanced so far; both their exports and imports have been quite limited. Mined sulfur has been decreasing and recovered sulfur increasing. Most of the recovered sulfur recently has been derived from hydrodesulfurization of heavy oil (Table 2.3). The price of sulfur has decreased with the increase in recovered sulfur.

The production of sulfuric acid from pyrite has been declining while that from smelter gas has expanded. Since 1970, the use of sulfur for production of the acid has been prohibited by the government and has been permitted only for one company. The acid by-produced from desulfurization of waste gas is not much yet. The demand for the acid is expected to increase by about 5% yearly.

Most of the gypsum supply in Japan has been derived from the by-product of wet-process phosphoric acid. About 60% of total gypsum has been used for retarder of cement setting and about 30% for plaster board. There was some oversupply of gypsum before 1970 but a little supply shortage has occurred after 1970 resulting in a price rise. Demand for gypsum is expected to continue to increase at a fairly high rate of 7-10% yearly. Most of the desulfurization plants to be built aim at the production of gypsum. Therefore, it is possible that a considerable oversupply will occur in future necessitating abandonment of a substantial amount of the by-produced gypsum or calcium sulfite unless some new uses are developed.

The supply of sodium sulfite has increased remarkably since 1967. Most of the increase is due to the by-product of waste-gas desulfurization. In 1970, about 50% of the sulfite was derived from the by-product. A considerable oversupply this year has caused price drops. Although the demand (mainly from paper mills) will continue to increase, not so many desulfurization plants to recover the sulfite will be built in future as was in the past.

10.2 Cost comparison of dry and wet processes for waste-gas desulfurization

The investment costs for major desulfurization plants are listed in Table 10.2.

Table 10.2 Investment costs for major desulfurization plants[14)]

Process	User	Plant site	Capacity (1,000scfm)	Cost (millions of dollars)
Dry process				
Hitachi (carbon)	Tokyo Electric	Kashima	250	5.45
Mitsubishi (manganese)	Chubu Electric	Yokkaichi	193	4.65
Sumitomo (carbon)	Kansai Electric	Sakai	100	2.75

Wet process				
Mitsubishi-JECCO	Kansai Electric	Amagasaki	59	1.46
Mitsubishi-JECCO	Tomakomai Chem.	Tomakomai	35	0.32
Wellman-Lord-MKK	Japan Synth. Rub.	Chiba	118	2.60
Showa Denko	Showa Denko	Kawasaki	88	0.81
Showa Denko	Ajinomoto	Kawasaki	159	1.79
Nippon Kokan	Nippon Kokan	Keihin	88	3.25
Mitsui-Chemico	Mitsui Aluminum	Omuta	226	3.25

The cost is generally cheaper for the wet process than for the dry process. Since usually about 70% of the desulfurization cost is accounted for by fixed cost including depreciation and interest, the wet process with reheating of gas is more economical than the dry process. The desulfurization cost with the dry process ranges from $1 to $1.2 per barrel of heavy oil or $1.6 to $1.9 per MWhr while the cost usually ranges from $0.8 to $1 per barrel of heavy oil or $1.2 to $1.6 per MWhr for the wet process. One of the common disadvantages to the wet process was the necessity of wastewater treatment. However, certain processes such as Mitsubishi-JECCO and Chiyoda have succeeded in eliminating of wastewater by balancing the water input for cooling, washing, etc. with the output by evaporation, hydration of gypsum, etc. On the other hand, the dry process is not always free from wastewater.

Thus the advantage of the wet process over the dry process has become clear. Major power companies formerly interested in the dry process have recently decided to build many desulfurization plants using the wet process (Table 4. 5).

10.3 Comparison of hydrodesulfurization, gasification desulfurization and flue-gas desulfurization

Figure 10.3 illustrates the relation between the desulfurization cost and sulfur content of products of topped-crude hydrodesulfurization and gasification desulfurization of heavy oil. The figure also illustrates the relation for flue-gas desulfurization; the desulfurization ratio is expressed in terms of the sulfur content of the oil for comparison.

By hydrodesulfurization it is not easy to reduce the sulfur in oil to below 1%. Although it may be possible to reduce it to 0.5%, the cost would increase substantially. By gasification desulfurization, sulfur can be reduced to below 0.1% but the cost is fairly high as was described in 3.1. Flue-gas desulfurization, especially that by the wet process, is advantageous in that it is available at low cost and for high removal of SO_2. One of the advantages to the desulfurization processes for oil is that elemental sulfur is recovered. By some flue-gas desulfurization processes such as the Wellman-Lord-Power Gas process of the U.S.A. and the MHI-IFP process, SO_2 can be converted to elemental sulfur. Although the desulfurization cost may be higher than with flue-gas desulfurization processes that by-produce gypsum, etc., it might be less than with gasification desulfurization. Another advantage to oil desulfurization processes is that the product oil or gas, with a low sulfur content, can be supplied not only to power plants but also to miscellaneous small plants and buildings where flue-gas desulfurization cannot be carried out economically. It seems logical, therefore, that large consumers of fuel such as power plants use flue-gas desulfurization and small consumers use low-sulfur fuel produced by desulfurization of oil.

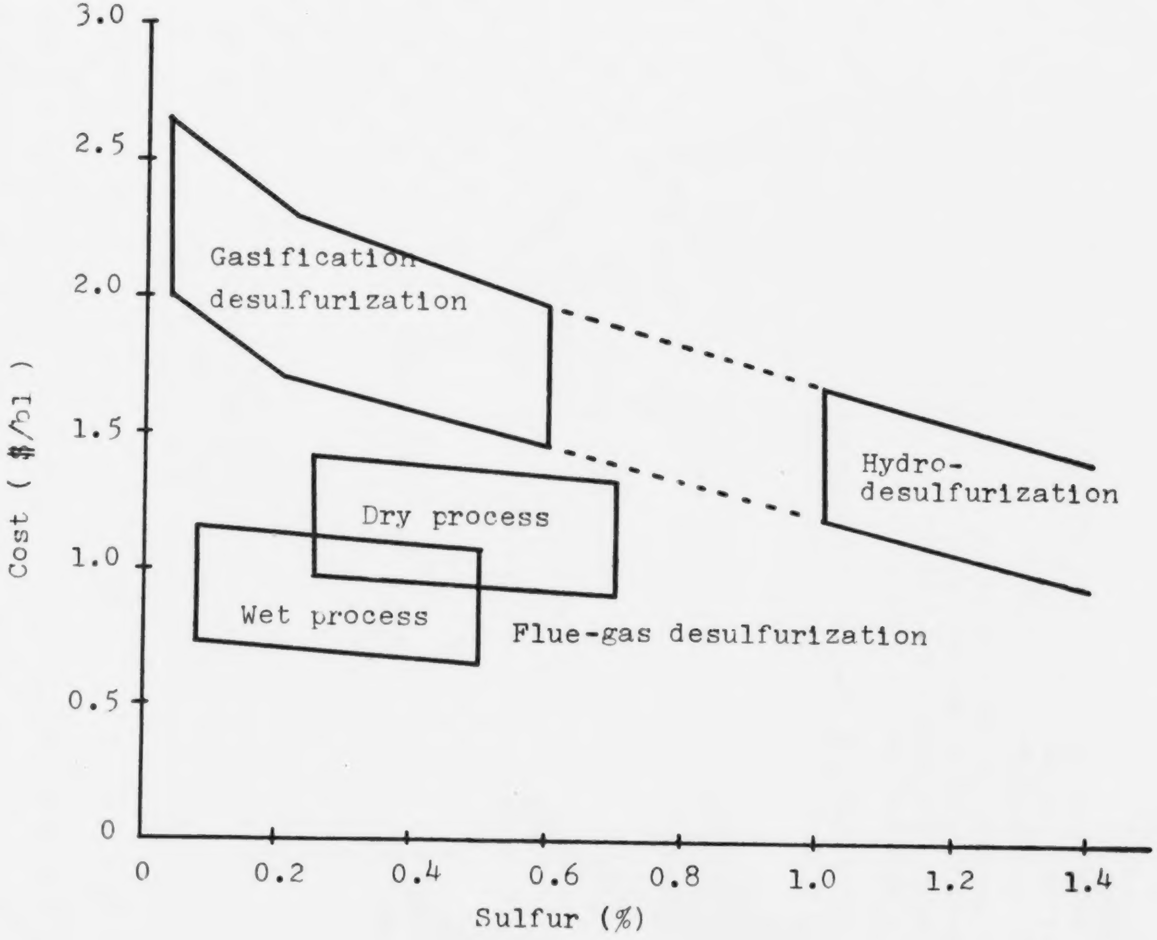


Figure 10.3 Comparison of desulfurization costs

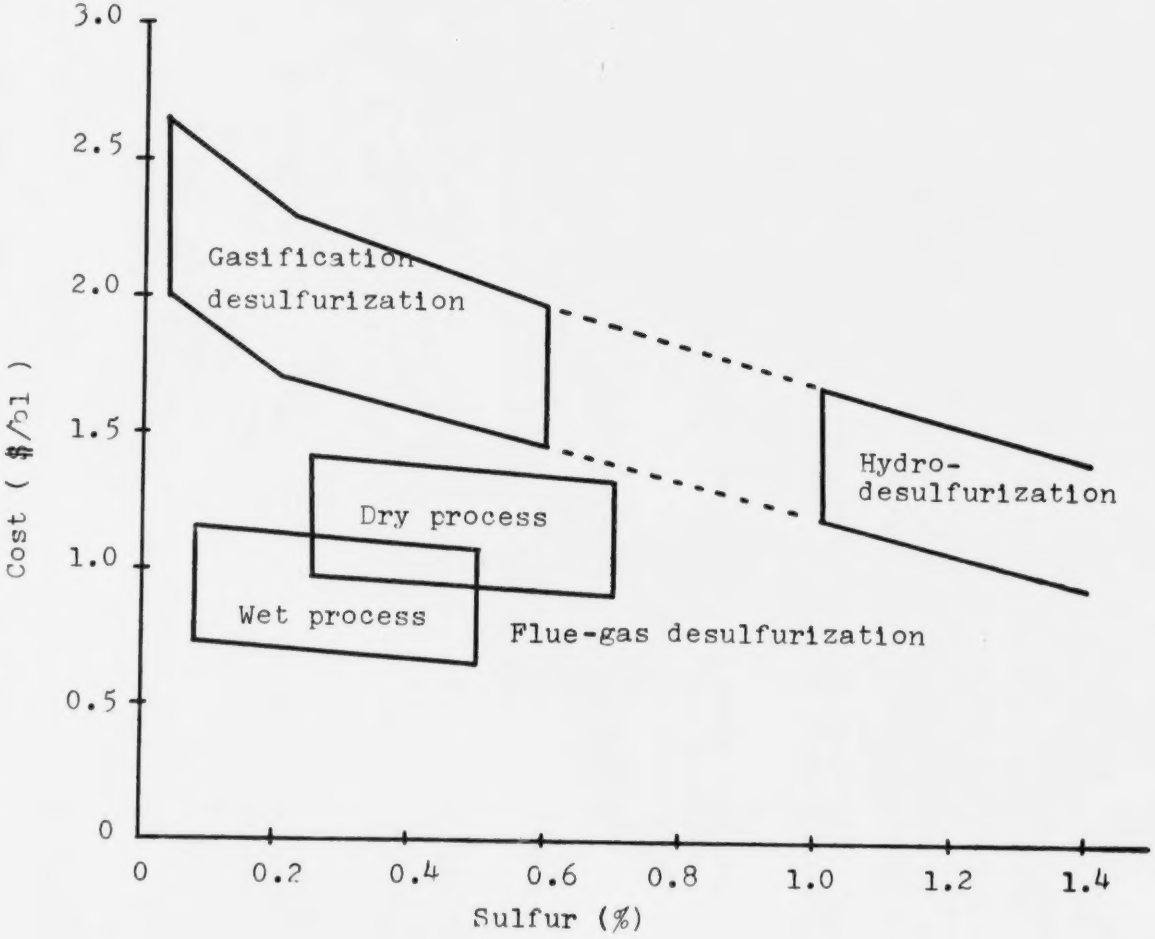


Figure 10.3 Comparison of desulfurization costs

11 Significance of application in U.S.A. of waste-gas desulfurization processes developed in Japan

11.1 Difference in circumstances

There are considerable differences in circumstances between the U.S.A. and Japan which should be realized in evaluating the Japanese processes for application in the U.S.A. The main differences are as follows:

(1) In the U.S.A., gypsum and sulfur from natural sources are plenty and cheap while these are quite limited in Japan. By-products from desulfurization can be sold for a good price in Japan, which fact is conducive to the development of the recovery processes.

(2) In the U.S.A., most plants have enough space to abandon waste products, while in Japan such space is quite limited necessitating maximum utilization of by-products.

(3) In the U.S.A., about 60% of electric power is generated by coal burning, which gives much fly ash. In Japan most power plants burn oil which gives little dust--an advantage in recovering by-products with high purity.

(4) In the U.S.A., many power plants are located far from chemical plants. In Japan power and chemical plants are usually close to each other; hence it is easy to utilize desulfurization by-products in chemical plants and also to use chemicals in power plants.

(5) In Japan many plants are close to cities. More than 90% removal of SO_2 or less than 100ppm SO_2 in emitted gas is usually required, while in the U.S.A. about 80% desulfurization or 300ppm SO_2 in the gas is usually acceptable.

These differences considerably affect the type of processes and design of the plants. For example, the sodium scrubbing process (to produce sodium sulfite) which has been most popular in Japan so far would not have as much chance for application in the U.S.A. Any Japanese process to be applied in the U.S.A. could be modified to suit better the local conditions in that country.

11.2 Wet-lime (limestone) process

Scaling problems As is well-known, scale formation has been the most baffling problem for the wet-lime process. However, three wet-lime process plants built in Japan recently have been free from scaling problems--they are Amagasaki plant, Kansai Electric (Mitsubishi-JECCO process), Onahama plant, Onahama Smelting (Mitsubishi-JECCO process), and Omuta plant, Mitsui Aluminum (Mitsui-Chemico process). The Amagasaki plant has been in operation for a year and a half treating flue gas from an oil-fired boiler containing 700-900ppm SO_2: the SO_2 concentration is much lower than in flue gas from coal-fired boilers in the U.S.A. The Onahama plant treats waste gas from a copper smelting furnace containing 20,000ppm SO_2 and has been in operation for four months since its start in late 1972. On the other hand, the Omuta plant treats flue gas from a coal-fired boiler containing fly ash and 1,300-2,000ppm SO_2, which is similar to U.S. flue gas. The power plant at Omuta, however, supplies electric power to aluminum reduction furnaces and the operation load does not change so much as with usual power stations. Thus conditions of these desulfurization plants may not be exactly the same as those typical in the U.S.A. However, the smooth operation of these plants seems to have proved that scaling is not an inevitable problem for the wet-lime process and can be prevented by proper plant design and operation. Operation of the plants including those under construction should be observed over longer periods to reach a final conclusion as to scaling.

Calcium sulfite or gypsum In Japan today, all desulfurization plants which use lime or limestone aim at the production of salable gypsum. Omuta plant of Mitsui Aluminum Co. (Mitsui-Chemico process) which has produced waste calcium sulfite will also convert the sulfite to salable gypsum. However, it is possible that in future a considerable amount of the by-product would be abandoned in the form of gypsum or calcium sulfite. In the U.S.A., conversely, all of the by-produced calcium sulfite is being abandoned now but it is possible that some plants which have not enough space for waste-ponds will produce either salable or throw-away gypsum.

By-produced gypsum from flue gas from coal-fired boilers can be used for gypsum board and cement if the fly ash content is reasonably low, as has been proved in the tests of Mitsui Miike Machinery with Mitsui Aluminum Co. (6.2). Even throw-away process gypsum has the following advantages over calcium sulfite: Gypsum does not increase the chemical oxygen demand of ambient water. Gypsum grows into much larger crystals than does the sulfite and precipitates easily into smaller volume thus reducing the required waste-pond size. In case of truck transportation of the by-products, gypsum can be handled much more easily because moisture content of the centrifuge discharge can be reduced to as low as 10%, while calcium sulfite is not easily filtered and the filter cake normally contains 60% of water. On the other hand, the disadvantage to the waste-gypsum process is that an oxidizer is required except in certain cases such as in Amagasaki Plant of Kansai Electric (6.1) and Kumagays Plant of Chichibu Cement (6.4), and also that gypsum is more soluble in water than calcium sulfite, although the latter may not be important.

Use of limestone and sulfuric acid Limestone scrubbing will be used in Yokosuka Plant, Tokyo Electric (Mitsubishi-JECCO process) and Mizushima Plant, Chugoku Electric (Babcock-Hitachi process). In both plants limestone in excess of stoichiometric will be used to attain high SO_2 removal, and thus some sulfuric acid will be required to convert the unreacted limestone to gypsum in order to obtain a salable product. For many power plants in the U.S.A., is may not be as convenient as in Japan to use sulfuric acid. When lime is used for absorbent, it is not necessary to use the acid because excessive lime is unneeded. In plants based on the Mitsubishi-JECCO lime-gypsum process, sulfuric acid is used on some occasions to lower the pH of calcium sulfite slurry in order to promote the oxidation into gypsum. It is not difficult, however,to maintain the pH of the slurry discharged from the absorber low enough for oxidation, particularly when the SO_2 concentration in the flue gas is relatively high (over 1,000ppm or so). If it is required to lower the pH, the acidic liquor formed in the prescrubber (or cooler with water sprays) can be used in place of sulfuric acid as has been carried out in the IHI-TCA process (6.4), although the by-product gypsum will be contaminated with dust. Even with the limestone-gypsum process it may be possible to eliminate the use of sulfuric acid, particularly when the SO_2 concentration in the gas is fairly high and 80-85% removal is satisfactory as in many power plants in the U.S.A. For example, Mitsui Miike Machinery Co., at the pilot plant operation as described in 6.5.2, has used a catalyst which is said to promote not only the reaction between SO_2 and limestone but also the oxidation of calcium sulfite obviating the use of sulfuric acid to produce salable gypsum.

11.3 Double-alkali process

The following three types of double-alkali process have been developed in Japan:

Sodium-lime	Nippon Steel Chemical, Hitachi Ltd.
Sodium-limestone	Kureha-Kawasaki, Showa Denko
Ammonia-lime	Nippon Kokan, Kurabo

The main problem with the sodium processes is the difficulty of conversion of sodium sulfate (formed by oxidation of the sulfite) to gypsum. A relatively weak solution has been used by Nippon Steel Chemical and also by Hitachi to optimize the conversion, resulting in the circulation of relatively large amounts of liquor. By the sodium-limestone processes of Kureha-Kawasaki and Showa Denko, sulfuric acid is required for the conversion. Where cheap sulfuric acid is available, the limestone process might be more economical than the lime process because of the cheapness of limestone. With the limestone process, crystals of calcium sulfite grow fairly well so that the filter cake has less moisture and is easy to handle for transportation. This may be an advantage when these processes are applied in the U.S.A. to produce throw-away calcium sulfite which has to be carried by trucks because of a lack of space to build a waste-pond nearby.

With the ammonia process it is much easier to convert the sulfate solution to gypsum. Moreover, ammonia is much cheaper than caustic soda. A common disadvantage to the various ammonia processes, however, is the plume problem.

Amagasaki Plant, Mitsubishi Electric Co. (Kurabo process) features very light plume (5.12). Although the plant is relatively small and uses a dilute liquor at low temperature, operation of the plant might indicate that the plume problem may not be unavoidable in ammonia scrubbing. The tests at Nippon Kokan also indicated that the plume problem could be solved (5.5). If so, the ammonia-lime process would be advantageous over the sodium-lime process.

Although the double-alkali processes in general feature freedom from scaling, it is less simple than the wet-lime or wet-limestone process. The consumption of some alkali is another drawback. If plant based on the wet-lime and wet-limestone processes could be operated without the scaling problem, the double alkali process might lose its raison d'être. It will take, however, some time to reach a conclusion about the significance of the processes.

11.4 Other major processes with gypsum by-production

There are two other major processes which by-produce gypsum--the Hitachi carbon process and the Chiyoda dilute sulfuric acid process. Although the absorbents as well as the reactions are entirely different, they have some common features in by-producing dilute sulfuric acid which is then reacted with limestone, in the ease of scale-free plant operation, and in the use of fairly large absorbers.

When flue gas from a coal-fired boiler is treated, the fly ash would pose a problem in the carbon step, even though most of the ash could be removed by a prescrubber. The Chiyoda process is said to work satisfactorily in treating coal-fired gas. As dilute sulfuric acid has a small capacity of SO_2 absorption, the Chiyoda process may suit better the treatment of gases with a relatively low SO_2 concentration, unlike the wet-lime or limestone process by which a higher desulfurization ratio is reached more easily with higher concentrations of SO_2. The elimination of wastewater is an advantage to the Chiyoda process, as well as of the Mitsubishi-JECCO process.

11.5 Processes to regenerate SO_2

There are many processes by which the absorbed SO_2 is regenerated for higher concentration by heating or by reduction. These processes are classified in the following way based on the absorbents:

Sodium scrubbing	Wellman-MKK, Wellman-SCEC
Magnesium scrubbing	Mitsui Mining, Onahama Smelting, Chemico-Mitsui, Kawasaki, Mitsui-Grillo
Carbon absorption	Sumitomo Shipbuilding
Cupric oxide	Shell
Ammonia scrubbing	MHI-IFP

Commercial plants constructed by MKK and SCEC in 1971 based on the Wellman-Lord process have been in smooth operation, demonstrating the reliability of the process. One problem with this process that calls for solution is the emission of wastewater containing sodium sulfate. The use of an oxidation inhibitor by SCEC is useful in reducing the sulfate but further improvement is desired.

Magnesium scrubbing processes also involve the problem of oxidation of a portion of magnesium sulfite into sulfate which is soluble in water and is not as easy as the sulfite to be thermally decomposed. Where there is some demand for magnesium sulfate, the Mitsui Mining process (7.2) may be useful. The use of the sulfate, however, is very limited.

The Kawasaki process features the production of filterable magnesium sulfite. The Mitsui-Grillo process is characterized by the use of magnesium with a small amount of manganese which promotes the SO_2 recovery and also thermal decomposition of magnesium sulfate. These two processes have been tested in pilot plants; there is no definite plan yet to build larger plants.

The Sumitomo carbon process is characterized by a smooth and safe operation and also by the fact that it gives no wastewater. The decrease of carbon consumption as well as the production of cheaper activated carbon is desired for the improved economics of the process.

The commercial plant by the Onahama process (7.3) has been on-stream since the end of 1972 but no detailed information has been released yet. With the Shell and MHI-IFP processes middle size commercial plants are under construction both of which will by-produce elemental sulfur by the reaction of regenerated SO_2 with H_2S. Operation data of these plants would be useful in further evaluation of the processes.

11.6 Other processes

11.6.1 Sodium scrubbing

Sodium scrubbing with by-production of sodium sulfite has been the most popular way of SO_2 recovery in Japan since sodium sulfite has been sold to paper producers for a reasonable price. Sodium scrubbing by-producing waste solution of sodium sulfite or sulfate has recently been used in many plants which emit smaller amounts of SO_2, because this is the easiest way of SO_2 removal. Also in the U.S.A. there may be many plants to which the sodium scrubbing processes may be conveniently applied.

11.6.2 Processes with by-production of ammonium sulfate

Yokkaichi plant of Chubu Electric (DAP-Mn process) has solved some problems encountered at the beginning and is now on-stream fairly well. Ammonium sulfate by-produced in this process, however, may not be a good product for most power stations in the U.S.A. Where the sulfate is useful, it may be by-produced more economically with ammonia scrubbing of flue gas, provided that the plume problem can be solved.

11.6.3 H_2S recovery processes

The Takahax, Fumaks, and Fumaks-Rhodacs processes have been adopted recently in many plants in Japan mainly for H_2S removal from coke oven gas because higher recovery is attained at lower cost than by conventional processes. The Takahax process features a broad applicability; H_2S in various waste gases can also be removed efficiently. Powdered sulfur by-produced in the Takahax and Fumaks processes, would be useful for agricultural chemicals. The Fumaks-Rhodacs combination process features the simultaneous recovery of H_2S, HCN and NH_3 in the gas. These processes may be useful also in the U.S.A.

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The descriptions in the present report are based primarily on the author's visits to the desulfurization plants, discussions with the users and developers of each process and also on data made available by them. In addition, the following publications have been used as references:

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